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Report No. 10

on

Contract No. N6onr-22524

Harold Shechter

25 March 1954

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Report No. 10

RF Proj. 396

R E P O R T

by

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

Columbus 10, Ohio

COOPERATOR: OFFICE OF NAVAL RESEARCH
Contract No. N6onr-22524

INVESTIGATION OF: Research in Nitromonomers and Their
Application to Solid Smokeless
Propellants

SUBJECT OF REPORT: Status Report for the Period
March 1, 1953 - March 1, 1954

SUBMITTED BY: L. Zeldin, D. Ley, E. Roberson,
D. Brain, T. Moritsugu and H. Shechter

DATE: March 25, 1954

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ABSTRACT

1. Reaction of 1-bromo-1,1-dinitroethane and sodium diethyl malonate in absolute ethanol at 5-10° yields sodium 1,1-dinitroethane (77%), tetraethyl ethane 1,1,2,2-tetracarboxylate (66%) and sodium bromide (100%). Piperidine and 1-chloro-1,1-dinitroethane in anhydrous ether at room temperature react to give piperidinium 1,1-dinitroethane (48.6%), piperidinium chloride (20.6%), 1-chloro-1,1-dinitroethane (6.5%, recovery) and unidentified products. It is concluded that the principal reaction of organic bases with 1-halo-1,1-dinitroalkanes results in displacement on "positive" halogen rather than on "positive" nitro groups or in elimination of nitrous acid.

2. Homogeneous reaction of silver 1,1-dinitroethane and silver 1,1-dinitropropane with ortho-nitrobenzene sulfonyl chloride in acetonitrile at 10-30° results in formation of ortho-nitrophenyl 1,1-dinitroethyl sulfide and ortho-nitrophenyl 1,1-dinitropropyl sulfide, readily crystallizable solids, in excellent yields. This reaction, an extension of that of Kharasch, is excellent for preparing solid derivatives of 1,1-dinitroalkanes. o-Nitrobenzenesulfonyl chloride has been found to offer advantage over 2,4-dinitrobenzenesulfonyl chloride.

3. 1-Methoxy-2-nitrobutane was prepared in 57% yield by reaction of methanol and 2-nitro-1-butene, catalyzed by sodium methoxide; oxidative nitration of 1-methoxy-2-nitrobutane yielded 1-methoxy-2,2-dinitrobutane (87%). Aniline and 2-nitro-1-butene react to give 2-nitro-1-phenylaminobutane (70%); 2,2-dinitro-1-phenylaminobutane (45%, isolated as the hydrochloride) was prepared by oxidative nitration of 2-nitro-1-phenylaminobutane. Reaction of 2-nitro-1-butene and ethanethiol, catalyzed by sodium methoxide, yielded ethyl 2-nitro-1-butyl thioether (84%); oxidative nitration of ethyl 2-nitro-1-butyl thioether to ethyl 2,2-dinitro-1-butyl thioether was unsuccessful.

Oxidative nitration of 4-nitropentanal and 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane resulted in 4,4-dinitropentanal (62%) and 1,1,1,2,2,3,3-heptafluoro-5,5-dinitroheptane (75%). Reaction of 1-bromo-2-phenylethane and silver nitrite yielded 1-nitro-2-phenylethane; 1,1-dinitro-2-phenylethane (55%) was prepared by reaction of sodium 1-nitro-2-phenylethane, sodium nitrite and silver nitrate. The physical properties of potassium- or of silver 1,1-dinitro-2-phenylethane have been determined. Oxidative nitration of nitrocyclopentane, 2,2-dimethyl-1-nitropropane and cyclohexylnitromethane produced dinitrocyclopentane (56%), 2,2-dimethyl-1,1-dinitropropane (56%, improved yield), and cyclohexyldinitromethane (70%, improved yield), respectively. Ethyl 3-nitrobutyrate (14%) was synthesized by reaction of silver nitrite and ethyl 3-bromobutyrate; ethyl 3,3-dinitrobutyrate (36%) was produced upon oxidative nitration of ethyl 3-nitrobutyrate.

4. Condensation of nitromethane and fluoral hydrate resulted in 1,1,1-trifluoro-3-nitro-2-propanol (83%); conversion of 1,1,1-trifluoro-3-nitro-

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2-propanol to 3-nitro-1,1,1-trifluoro-2-propyl acetate was effected in excellent yield by reaction with acetic anhydride and sulfuric acid. 3,3,3-Trifluoro-1-nitropropene (47%) was prepared by heating mixtures of phthalic anhydride and 1,1,1-trifluoro-3-nitro-2-propanol. 1-Nitro-2-trifluoromethyl-2-propanol (53%) was obtained upon condensation of nitromethane and 1,1,1-trifluoroacetone in the presence of potassium carbonate.

5. A study has been made of selective-reduction of conjugated nitroalkenes with sodium trimethoxyborohydride in ethyl ether-tetrahydrofuran at -40 to -70°. The compounds which have been reduced are: (1) 1-nitropropene, (2) 2-nitro-1-butene, (3) 2-nitro-2-butene, (4) omega-nitrostyrene, (5) 4-nitro-3-heptene, (6) 3,3,3-trichloro-1-nitropropene, (7) 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene and (8) 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene. The products which have been obtained are: (1) 1-nitropropane (81.7%) and 2-methyl-1,3-dinitropentane (11.4%), (2) 2-nitrobutane (45%) and 3-methyl-3,5-dinitroheptane (35%), (3) 2-nitrobutane (62.6%) and 3,4-dimethyl-2,4-dinitrohexane (11.4%), (4) 1-nitro-2-phenylethane (38.6%) and 1,3-dinitro-2,4-diphenylbutane (presumably as two racemates), (5) 4-nitroheptane (55%), (6) 1,1,1-trichloro-3-nitropropane (44.2%) and 1,1,1-trichloro-3,5-dinitro-4-trichloromethylpentane (32.1%), (7) 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (91%) and (8) 1,1,1,2,2,3,3-heptafluoro-5-nitrohexane (84%). 3-Methyl-3,5-dinitroheptane, 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane and 1,1,1,2,2,3,3-heptafluoro-5-nitrohexane were further identified as the 2,4-dinitrophenylhydrazones of 5-methyl-5-nitro-3-heptanone, 5,5,6,6,7,7,7-heptafluoro-3-heptanone and 4,4,5,5,6,6,6-heptafluoro-2-hexanone. 1,3-Dinitro-2,4-diphenylbutane was prepared also by Michael reaction of omega-nitrostyrene and 1-nitro-2-phenylethane.

4-Nitro-3-heptane was synthesized by the following sequence: (1) condensation of propanal and 1-nitrobutane in sodium hydroxide to yield 4-nitro-3-heptanol (77%), (2) conversion of 4-nitro-3-heptanol to 3-acetoxy-4-nitroheptane (89%) by reaction with acetic anhydride, and (3) reaction of 3-acetoxy-4-nitroheptane with sodium acetate to give 4-nitro-3-heptane (72.8%).

6. The selective-reduction of the carbon-carbon double bond of conjugated nitroolefins with lithium borohydride in ethyl ether and tetrahydrofuran has been investigated at -70 to -60°. The conjugated nitroolefins which have been studied are: (1) 1-nitropropene, (2) 2-nitro-1-butene, (3) 4-nitro-3-heptene, (4) 3,3,3-trichloro-1-nitropropene, (5) 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene, and (6) 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene. The reduction products and yields in these systems are: (1) 1-nitropropane (49.9%) and 2-methyl-1,3-dinitropentane, (2) 2-nitrobutane (59.3%) and 3-methyl-3,5-dinitroheptane (14.2%), (3) 4-nitroheptane (65%), (4) 1,1,1-trichloro-3-nitropropane (48.3%), (5) 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (91%) and (6) 1,1,1,2,2,3,3-heptafluoro-5-nitrohexane (87.8%). The structures of the reaction products were assigned on the bases of quantitative and infrared analyses, chemical properties, and conversion to appropriate derivatives.

7. A study has been initiated of the effectiveness of lithium aluminum

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hydride for selectively reducing the conjugated carbon-carbon double bond of α , β -nitroalkenes; the reactions are effected upon addition of solutions of the nitroolefin in ethyl ether-tetrahydrofuran to lithium aluminum hydride in ethyl ether-tetrahydrofuran at -70° . Reduction of 3,3,5-trichloro-1-nitropropene yielded 1,1,1-trichloro-3-nitropropane (43.8%); reduction of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene gave 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (85.3%).

8. Sodium borohydride in ethanol has been found to be an effective reagent for reducing conjugated nitroalkenes to nitroalkanes. D-xylo-tetraacetyl-1-nitrohexene has been reduced to 1-nitro-1,2-dideoxy-D-xylo-hexitol tetraacetate in 63.9% yield with sodium borohydride-ethanol at 0° . Heterogeneous reduction of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene with sodium borohydride in ethyl ether-tetrahydrofuran was unsuccessful.

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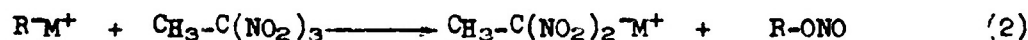
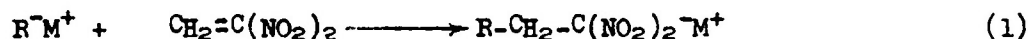
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DISCUSSION

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1. REACTION OF 1-BROMO-1,1-DINITROETHANE AND SODIUM DIETHYL MALONATE;
FORMATION OF SODIUM 1,1-DINITROETHANE AND TETRAETHYL ETHANE-
1,1,2,2-TETRACARBOXYLATE.

1,1,1-Trinitroethane has been found to undergo two general reactions¹ in the presence of bases: (1) elimination of nitrous acid from 1,1,1-trinitroethane by attack of one equivalent of the base to give 1,1-dinitroethylene as a possible intermediate (Equations 1); subsequent addition of the base to "1,1-dinitroethylene" yields the corresponding beta-substituted derivative of salts of 1,1-dinitroethane, and (2) attack of the base on 1,1,1-trinitroethane resulting in removal of a "positive nitro group" and yielding a salt of 1,1-dinitroethane; subsequent reaction of the base with the intermediate derived from interaction of the base and the nitronium group may result in displacement to give nitrite ion and the product derivable from oxidative-coupling of two of the basic anions (Equations 2).



Metal alkoxides,^{1a,b} potassium cyanide,^{1g,i} piperidine,^{1f,h} trimethylamine,^{1g,h} guanidine,^{1h,i,j} and potassium ethyl malonate,^{1d,h} react by elimination-addition according to Equations 1 to give beta-alkylated derivatives of 1,1-dinitronitroethane. Potassium 2-nitropropane,^{1a} potassium n-butyl mercaptide,^{1f} butyllithium,^{1g,i} and metallic hydroxides^{1a,b} undergo oxidation-reduction of the type of Equations 2. Attempts to alkylate 1,1,1-trinitroethane with potassium benzyl cyanide in the presence of ethanol¹ⁱ resulted in formation of potassium 2-ethoxy-1,1-dinitroethane (Equations 1). Potassium acetylacetonel^f reacted primarily via sequence 2 to give potassium 1,1-dinitroethane; however, evidence was obtained for the formation of 3-acetyl-5,5-dinitro-2-pentanone in minor amounts. Ambiguous results were obtained when triethylamine was used as the attacking base.^{1f}

The study of the reactions of bases and 1,1,1-trinitroethane has been extended to 1-bromo-1,1-dinitroethane and to 1-chloro-1,1-dinitroethane. The purposes in the extension of this research are: (1) to develop new and more convenient methods for preparation of 1,1-dinitroethylene in situ and of its addition products and (2) to obtain information concerning the behavior of 1-halo-1,1-dinitroethanes toward oxidative-reductive attack by various bases. It has been previously reported from this laboratory that piperidine reacts with 1-bromo-1,1-dinitroethane^{1i,j}

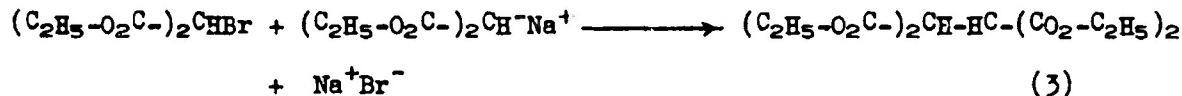
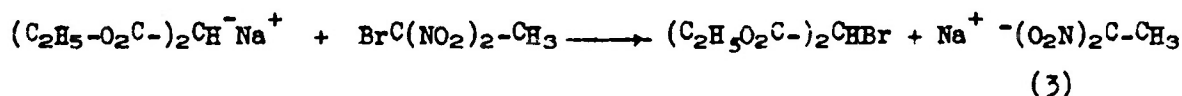
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in ethyl ether at 0° by the oxidation-reduction sequence (analogous to Equations 2) resulting in displacement of brominium ion to give piperidinium 1,1-dinitroethane (64.3%), piperidinium bromide (74.7%) and a high molecular weight product (presumably a trimer) derived from 3,4,5,6-tetrahydropyridine. In the present report from this laboratory there are described the results of the investigations of reaction of 1-bromo-1,1-dinitroethane with sodium diethyl malonate and of reaction of piperidine and 1-chloro-1,1-dinitroethane.

Reaction of sodium diethyl malonate and 1-bromo-1,1-dinitroethane (Equations 3) in absolute ethanol at 5-10° occurs fairly rapidly to give sodium bromide (100%), sodium 1,1-dinitroethane (77%) and tetraethyl ethane-1,1,2,2-tetracarboxylate (66%). There was no evidence for a reaction of the elimination-addition type to give potassium 2-carbethoxy-4,4-dinitrobutyrate^{1d,h} as was experienced with potassium diethyl malonate and 1,1,1-trinitroethane; it is of interest that attack of the diethyl malonate anion on 1-bromo-1,1-dinitroethane results in displacement of a positive bromine atom rather than a positive nitro group. An equation sequence (Equations 3) which accounts for formation of sodium bromide, sodium 1,1-dinitroethane, and tetraethyl ethane-1,1,2,2-tetracarboxylate is as follows:



The sodium 1,1-dinitroethane was identified upon isolation and upon conversion to 1,1-dinitroethane; the yield of sodium 1,1-dinitroethane produced in these experiments was determined quantitatively by use of ultraviolet methods. The tetraethyl ethane-1,1,2,2-tetracarboxylate was identified by its chemical and physical properties and by comparison with an authentic sample. The yield of sodium bromide was determined quantitatively by conversion to silver bromide. Attempts were made to isolate diethyl bromomalonate, a suspected intermediate in the coupling reaction; however, it could not be detected under the conditions of the experiments. On the basis of the results of the experiments of reactions of piperidine and sodium diethyl malonate with 1-bromo-1,1-dinitroethane, it is predicted that the principal reactions of 1-bromo-1,1-dinitroethane with bases will result in removal of positive bromine by mechanisms of the displacement type and that 1-bromo-1,1-dinitroethane does not offer the promise as does 1,1,1-trinitroethane for producing 1,1-dinitroethylene in situ.

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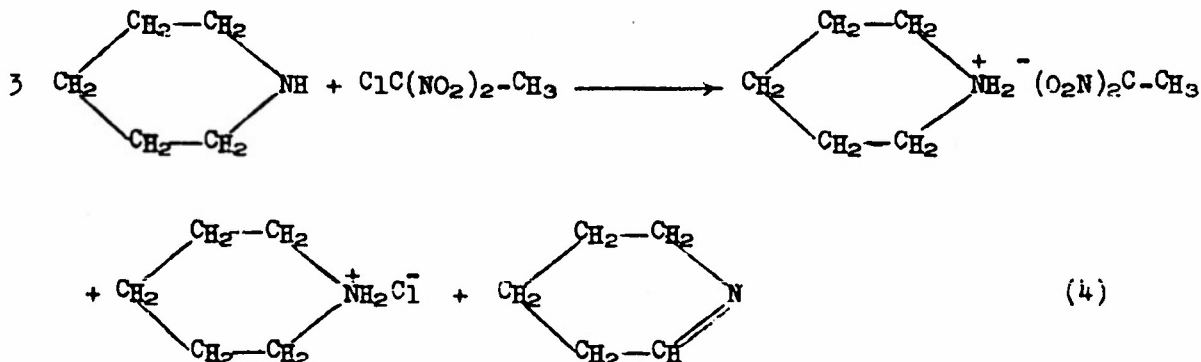
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2. REACTION OF PIPERIDINE AND 1-CHLORO-1,1-DINITROETHANE; FORMATION OF PIPERIDINIUM 1,1-DINITROETHANE AND PIPERIDINIUM CHLORIDE.

It has been previously found that piperidine^{1f,h} reacts with 1,1,1-trinitroethane by elimination-addition to yield N-(2,2-dinitroethyl)-piperidine and piperidinium nitrite, whereas reaction of piperidine with 1-bromo-1,1-dinitroethane^{1i,j} occurs by displacement on bromine to give piperidinium 1,1-dinitroethane, piperidinium bromide and 3,4,5,6-tetrahydropyridine (tent.). In an effort to develop new and more convenient methods for preparing "1,1-dinitroethylene" in situ and also to compare the general reactions of 1-halo-1,1-dinitroalkanes toward bases with those of 1,1,1-trinitroethane, the reactions of piperidine and 1-chloro-1,1-dinitroethane have been investigated.

1-Chloro-1,1-dinitroethane² was prepared by reaction of chlorine and sodium 1,1-dinitroethane. Reaction of 1-chloro-1,1-dinitroethane with piperidine in anhydrous ethyl ether occurred slowly (Equations 4) at room temperature to give piperidinium 1,1-dinitroethane (48.6% yield), piperidinium chloride (20.6% yield), 1-chloro-1,1-dinitroethane (6.5% yield), and unidentified products (presumably derived from chlorination and dehydrochlorination of piperidine); N-(2,2-dinitroethyl)-piperidine, the product expected from elimination-addition, was not obtained from this reaction.



Piperidinium 1,1-dinitroethane was detected and determined quantitatively by ultra-violet spectrophotometric methods; the salt was also compared with an authentic sample prepared by reaction of piperidine and 1,1-dinitroethane. The yield of piperidinium chloride was ascertained from the water-soluble products by precipitation of the chloride ion as silver chloride. It is to be concluded from this experiment as well as those with 1-bromo-1,1-dinitroethane that reaction of 1-halo-1,1-dinitroethanes with appropriate bases involve attack on halogen rather than elimination of hydrogen halide (or of nitrous acid) to give 1,1-dinitroethylene (or 1-chloro-1-nitroethylene) or its subsequent adducts. Further studies of this apparent generalization with 1-halo-1,1-dinitroethanes are now in progress.

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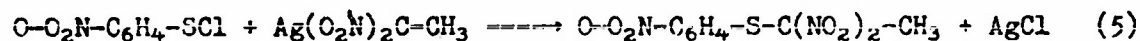
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3. DISPLACEMENT REACTIONS OF SILVER SALTS OF 1,1-DINITROETHANE AND OF 1,1-DINITROPROPANE WITH ORTHO-NITROBENZENE SULFENYL CHLORIDE.
SYNTHESIS OF ORTHO-NITROPHENYL 1,1-DINITROETHYL SULFIDE AND ORTHO-NITROPHENYL 1,1-DINITROPROPYL SULFIDE.

Reaction of alkyl halides with metallic salts of mononitroalkanes³ may result in carbon-alkylation to yield substituted mononitroalkanes or in oxygen-alkylation to give nitronic esters or their decomposition products (oximes and carbonyl compounds); in general, the principal reaction is that involving attack on oxygen. On the other hand, salts of mononitroalkanes undergo rapid displacement reactions with aryldiazonium halides⁴ or with arylsulfenyl halides⁴ to give the carbon-alkylated derivatives, arylazonitroalkanes and aryl nitroalkyl sulfides, in good yields.

Upon studying displacement reactions of alkyl halides with electrovalent salts of 1,1-dinitroalkanes, it has been found that there are certain similarities in results with those obtained from salts of mononitroalkanes and alkyl halides in that the principal reaction is one involving oxygen-alkylation; the minor reaction is that in which substituted gem-dinitroalkanes are formed. In using covalent salts of 1,1-dinitroalkanes^{1,2,3} such as silver 1,1-dinitroethane heterogeneously or in solution in acetonitrile, it was found that carbon-alkylation could be enhanced; however, the reaction gave little promise as an excellent method for preparing substituted gem-dinitroalkanes. As part of a general program for developing new carbon-alkylation reactions of salts of 1,1-dinitroalkanes, as part of a study of the structural natures of cations which effect selectivity in carbon-alkylation of nitronate ions, and as part of a general study for developing methods for preparing solid derivatives of 1,1-dinitroalkanes, a study has been initiated of the displacement reactions of benzenesulfenyl halides and of aryldiazonium halides with salts of 1,1-dinitroalkanes. The results of the present studies of reactions of ortho-nitrobenzenesulfenyl chloride with silver 1,1-dinitroethane and with silver 1,1-dinitropropane are now reported.

Reactions of silver 1,1-dinitroethane and silver 1,1-dinitropropane in acetonitrile (homogeneous) with ortho-nitrobenzenesulfenyl chloride occurs almost instantaneously to yield ortho-nitrophenyl 1,1-dinitroethyl sulfide (Equation 5) and ortho-nitrophenyl 1,1-dinitropropyl sulfide along with silver chloride. The products of reaction are stable solids



and are readily crystallized; they serve as excellent solid derivatives of 1,1-dinitroalkanes. The proofs of structure of these compounds have not yet been completed, but, on the basis of the previous establishments of structure of similar derivatives prepared from mononitroalkanes^{4b}

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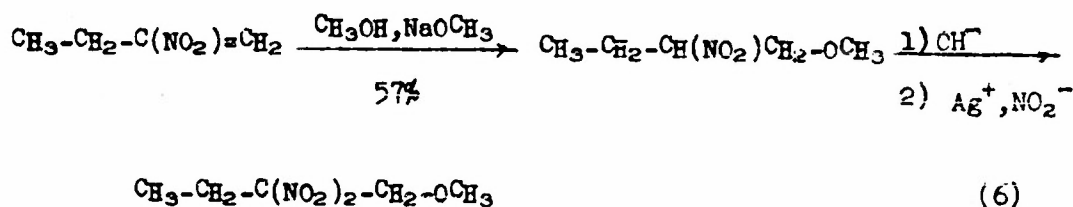
it seems quite likely that the derivatives obtained from 1,1-dinitroalkanes are true aryl 1,1-dinitroalkyl sulfides.

4. STUDIES OF OXIDATIVE-NITRATION OF SUBSTITUTED MONONITROALKANES;
PREPARATION OF 1-METHOXY-2,2-DINITROBUTANE, 2,2-DINITRO-1-PHENYLAMINO-
BUTANE, 4,4-DINITROPENTANAL, 1,1,1,2,2,3,3-HEPTAFLUORO-5,5-DI-
NITROHEPTANE, 1,1-DINITRO-2-PHENYLETHANE, ETHYL 3,3-DINITROBUTYRATE,
DINITROCYCLOPENTANE, CYCLOHEXYLDINITROMETHANE (IMPROVED YIELD), A)
2,2-DIMETHYL-1,1-DINITROPROPANE (IMPROVED YIELD).

Studies of the scope of oxidative-nitration^{1d-1,2,6} of primary and secondary mononitroalkanes have been continued. It is the purpose of the present research to determine the effects of various functional groups on the course and on the efficiency of the oxidative-nitration reaction; it is also expected to obtain further information concerning the chemical and physical properties of substituted gem-dinitroalkanes.

It has been previously demonstrated that non-branched 2-nitro-1-alkanols^{6,7} and 3-nitro-2-butanol^{6,7} may be converted to 2,2-dinitro-1-alkanols and 3,3-dinitro-2-butanol by careful use of oxidative-nitration techniques. It has also been found previously⁶ that electronegatively-substituted α,β -systems such as methyl nitroacetate, nitroacetonitrile, nitroacetone, and 3-nitropropene are not converted into the corresponding gem-dinitroalkanes by oxidative-nitration methods. In order to obtain further information concerning the possibility of nitrating other types of nitroalkanes which are substituted in the beta-position with functional groups, a study has been made of oxidative-nitration of 1-methoxy-2-nitrobutane, 2-nitro-1-phenylaminobutane, and ethyl 2-nitro-1-butyl thioether.

1-Methoxy-2-nitrobutane (Equations 6) was prepared in 57% yield by addition of methanol and 2-nitro-1-butene at room temperature in the presence of sodium methoxide. Reaction of 1-methoxy-2-nitrobutane with sodium hydroxide in water-methanol at 0° and subsequent treatment of the reaction mixture with sodium nitrite and silver nitrate gave 1-methoxy-2,2-dinitrobutane as a stable liquid in 87% yield. The assignment of structure of 1-methoxy-2,2-dinitrobutane was based on its quantitative and infrared analyses, its molar refraction, and its chemical and physical properties.

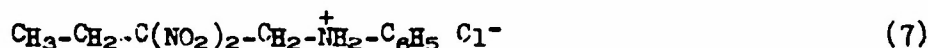
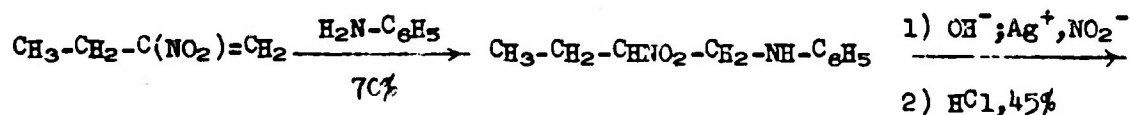


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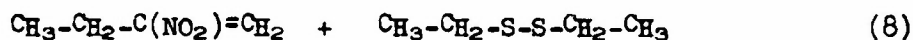
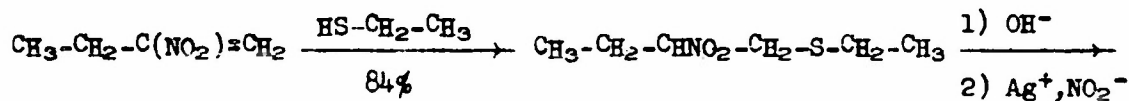
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2-Nitro-1-phenylaminobutane (Equations 7) was synthesized by reaction of 2-nitro-1-butene and aniline at temperatures below 30°; the initial adduct was best isolated as the crystalline hydrochloride. Reaction of 2-nitro-1-phenylaminobutane hydrochloride with dilute sodium carbonate and subsequent distillation gave pure 2-nitro-1-phenylaminobutane in 70% yield. The identity of 2-nitro-1-phenylaminobutane was established from its analysis, from its infrared spectrum, from its molecular refraction, and from its reaction with hydrogen chloride. Oxidative-nitration of 2-nitro-1-phenylaminobutane was effected satisfactorily to yield 2,2-dinitro-1-phenylaminobutane (45% yield); the 2,2-dinitro-1-phenylaminobutane was isolated, purified, analyzed, and identified as 2,2-dinitro-1-phenylaminobutane hydrochloride.



Ethyl 2-nitro-1-butyl thioether (Equations 8) was obtained in 84% yield from addition of ethanethiol to 2-nitro-1-butene in methanol, catalyzed by sodium methoxide. The quantitative and infrared analyses of the thioether are in agreement with the structure proposed for the adduct. Attempts to effect oxidative-nitration of ethyl 2-nitro-1-butyl thioether to ethyl 2,2-dinitro-1-butyl thioether, as yet, have all been unsuccessful. Silver deposition occurs as in the usual oxidative-nitration reaction; however, the principal product of reaction is 2-nitro-1-butene. The formation of 2-nitro-1-butene is not due to base-catalyzed decomposition of salts of ethyl 2-nitro-1-butyl thioether; it is apparent that the 2-nitro-1-butene is formed during the oxidation-reduction steps. Further studies of systems of this type are in progress.



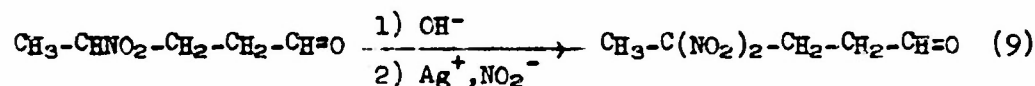
The oxidative-nitration reaction of 4-nitro-1-pentanal has been investigated in order to determine if oxidative-nitrations may be effected selectively in nitro compounds containing aldehyde groups; in general, aldehydes are converted to their corresponding carboxylic acids upon reaction with silver oxidants. It has now been found that oxidative-nitration of 4-nitropentanal may be effected at 0° to give 4,4-dinitropentanal (Equation 9) in 62% yield; 4,4-dinitropentanal⁹ was characterized

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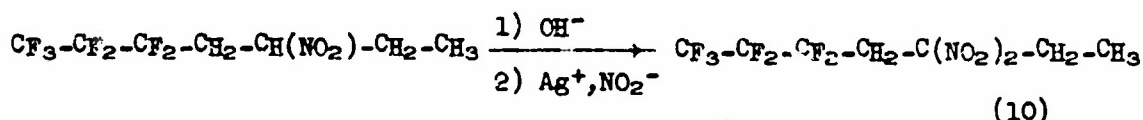
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as its semicarbazone⁹ and its p-nitrophenylhydrazone.⁹

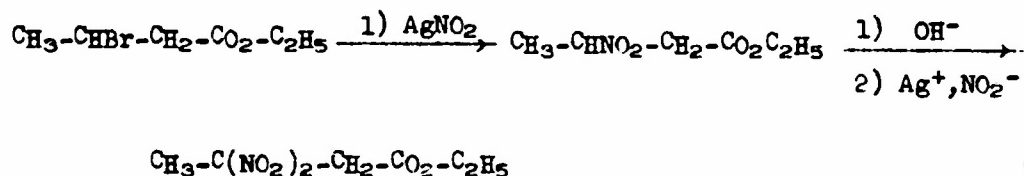
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The oxidative-nitration reaction has been extended to the preparation of highly fluorinated gem-dinitroalkanes. 1,1,1,2,2,3,3-Heptafluoro-3-nitroheptane was prepared by reduction of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene with various complex hydrides¹⁰; oxidative nitration gave 1,1,1,2,2,3,3-heptafluoro-5,5-dinitroheptane as a stable colorless liquid in 75% yield. The dinitroheptafluoroheptane was identified by its quantitative and infrared analyses and its chemical and physical properties.



The oxidative-nitration reaction has been extended to 1-nitro-2-phenylethane, nitrocyclopentane, and ethyl 3-nitrobutyrate; improved procedures have been developed for preparation of cyclohexyldinitromethane and for 2,2-dimethyl-1,1-dinitropropane. 1-Nitro-2-phenylethane was prepared in 44% yield from silver nitrite and 1-bromo-2-phenylethane; its conversion to 1,1-dinitro-2-phenylethane was effected in 55% yield. 1,1-Dinitro-2-phenylethane, a crystalline solid, was identified by its quantitative and infrared analyses; it was characterized as its potassium and silver salts (the properties of these salts have been determined). Oxidative-nitration of nitrocyclopentane occurs rapidly to give dinitrocyclopentane in 56% yield. Ethyl 3-nitrobutyrate (Equations 11) was synthesized by reaction of silver nitrite and ethyl 3-bromobutyrate (25%); it is quite difficult to remove all nitrite and nitrate impurities in systems of this type, however, the ethyl 3-nitrobutyrate could be isolated in analytical purity by repeated rectification of the reaction product. Ethyl 3,3-dinitrobutyrate was obtained in 36% yield by oxidative-nitration of ethyl 3-nitrobutyrate in aqueous methanol; the dinitro ester is a stable liquid which can be readily purified by distillation.



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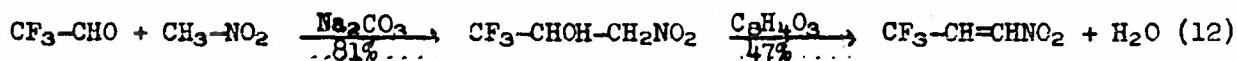
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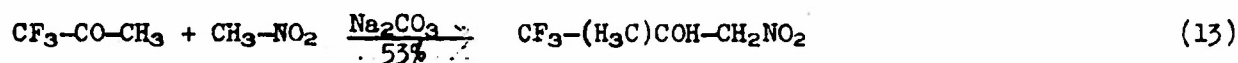
5. PREPARATION AND STUDIES OF POLYFLUOROPOLYNITROALKANES, SYNTHESIS OF 1,1,1-TRIFLUORO-3-NITRO-2-PROPANOL, 3,3,3-TRIFLUORO-1-NITROPROPENE, AND 1-NITRO-2-TRIFLUOROMETHYL-2-PROPANOL.

A program has been initiated of synthesis of 1,1,1-trifluoro-3,3-dinitropropane, 1,1,1,2,2,3,3-heptafluoro-5,5-dinitropentane, 1,1,1-trifluoro-2-methyl-3,3-dinitropropane, 1,1,1-trifluoro-2,2-dimethyl-3,3-dinitroethane, and 2,2-bis-(trifluoromethyl)-1,1-dinitropropane. The purpose of this study is, (1) to extend the oxidative-nitration reaction to the preparation of highly fluorinated polynitroalkanes, (2) to obtain general information concerning the thermal and explosive properties of polyfluoropolynitroalkanes, and (3) to determine the ionization constants of fluorinated 1,1-dinitroalkanes and the ultraviolet spectra and solubilities of their potassium salts; it is believed that decisive results might be obtained from this study which will substantiate the hypothesis¹¹ that there is limited resonance stabilization in anions derived from highly hindered 1,1-dinitroalkanes.

In the present study there is reported the synthesis of 1,1,1-trifluoro-3-nitro-2-propanol, 3,3,3-trifluoro-1-nitropropene and 1-nitro-2-trifluoromethyl-2-propanol. Cook, et al¹⁰ have previously prepared 1,1,1-trifluoro-3-nitro-2-propanol in 47% yield by condensation of trifluoroacetaldehyde and nitromethane (Equation 12). In the present study, condensation of nitromethane and trifluoroacetaldehyde in the presence of potassium carbonate to give 1,1,1-trifluoro-3-nitro-2-propanol has been effected in 81% yield; the improved procedure results from using nitromethane and trifluoroacetaldehyde in a mole ratio 3 to 1. 1,1,1-Trifluoro-3-nitro-2-propanol was converted to 3,3,3-trifluoro-1-nitropropene (Equation 12) in 47% yield upon being heated at 140° with phthalic anhydride; attempts to prepare 3,3,3-trifluoro-1-nitropropene by reaction of sodium carbonate and 1,1,1-trifluoro-3-nitro-2-propyl acetate, prepared from acetic anhydride and 1,1,1-trifluoro-3-nitro-2-propanol, were unsuccessful.



Condensation of nitromethane and 1,1,1-trifluoroacetone (mole ratio 3:1) in the presence of anhydrous potassium carbonate results in formation of 1-nitro-2-trifluoromethyl-2-propanol (Equation 13) in 53% yield. Complete results of the conversions of 1-nitro-2-trifluoromethyl-2-propanol to 1-nitro-2-trifluoromethyl-1-propene will be summarized in a subsequent report.



6. SELECTIVE REDUCTION OF CONJUGATED NITROOLEFINS WITH LITHIUM BORHYDRIDE, NITROALKANES.

It has been previously reported^{11,14} that the conjugated double bond of the nitroolefins: 1-nitropropene, 2-methyl-1-nitropropene, 2-nitro-1-butene, and

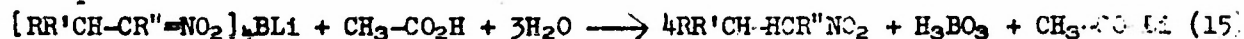
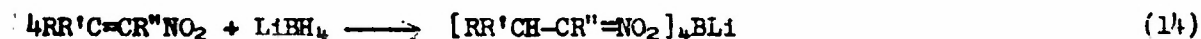
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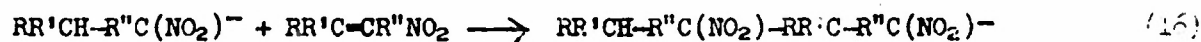
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omega-nitrostyrene can be selectively reduced by lithium borohydride in ethyl ether-tetrahydrofuran at -40 to -70° (Equation 14 and 15). The reaction



is complicated by consecutive processes of the Michael type in which the reduction product adds to the initial conjugated nitroolefin to yield the corresponding 1,3-dinitroalkanes (Equation 16). It has been found, however,



that reduction may be effected satisfactorily, with respect to speed and completion of reaction and to minimization of consecutive Michael addition, by adding the nitroolefin to 100 per cent excess of reducing agent at controlled temperatures. On the basis of the results obtained, it is suggested that steric factors become greatly increased as each nitronate ion becomes complexed with the borohydride ion and thus the reducing potential of the species formed, trialkylnitronatoborohydride and dialkylnitronatoborohydride ions, are greatly diminished.

Herein are reported the final completed experiments¹¹ for reduction of 1-nitropropene and 2-nitro-1-butene with lithium borohydride. The reductions of 4-nitro-3-heptene, 3,3,3-trichloro-1-nitropropene, 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene and 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene have also been conducted to give the corresponding saturated nitroalkanes in 65, 85, 87.8 and 91% yields, respectively. It is apparent that reduction of the fluorinated nitroolefins is facilitated by the inductive effect of the perfluoroalkyl groups. The reduction products were identified by their physical constants, infrared spectra; and by conversion to the corresponding carbonyl compounds via the Nef reaction and thence to their 2,4-dinitrophenylhydrazones. It has been previously reported¹⁰ that fluorinated nitroalkanes do not undergo Nef reactions to yield perfluoroalkyl alkyl ketones; it is of importance that under the conditions used in the present investigation 1,1,1-2,2,3,3-heptafluoro-5-nitrohexane and 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane are converted to 4,4,5,5,6,6,6-heptafluoro-2-hexanone and 5,5,6,6,7,7,7-heptafluoro-3-heptanone, respectively, under the conditions of the Nef reaction.

4-Nitro-3-heptene, a new compound, was synthesized by the following sequence: (1) condensation of propanal and 1-nitrobutane in the presence of sodium hydroxide gave 4-nitro-3-heptanol (77%), (2) reaction of 4-nitro-3-heptanol with acetic anhydride yielded 3-acetoxy-4-nitroheptane (89%); and (3) conversion of 3-acetoxy-4-nitroheptane to 4-nitro-3-heptene, effected by sodium acetate in 73% yield. Reduction of 4-nitro-3-heptene, a relatively hindered nitroalkene, has demonstrated the importance of keeping the temperature of reaction below 0° ; reduction at 0° gave, in addition to 4-nitrohep-

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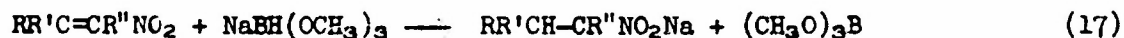
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tane (45%), a complex mixture (20%) which exhibited infrared absorption for hydroxyl and amine groups. It is apparent that reduction of the nitro group, possibly to an oxime, a hydroxylamine, or an amine, has been effected; further study of this reaction is in progress.

7. SELECTIVE REDUCTION OF CONJUGATED NITROOLEFINS WITH SODIUM TRIMETHOXYBOROHYDRIDE; NITROALKANES.

Selective reduction of the carbon-carbon double bond of the conjugated nitroolefins: 1-nitropropene, 2-methyl-1-nitropropene, 2-nitro-1-butene and 2-nitro-2-butene with sodium trimethoxyborohydride in ethyl ether-tetrahydrofuran has been reported previously from this laboratory.⁴ The reduction proceeds by hydride transfer according to Equations 17 and 18; a secondary reaction occurs by addition of the anion of the reduced product to the nitroolefin to yield the corresponding 1,3-dinitroalkane (Equation 19, Michael addition).



Herein are reported the final experiments for reduction of 1-nitropropene and 2-nitro-1-butene. It is also reported that extension of the reduction reaction to omega-nitrostyrene, 4-nitro-3-heptene, 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene, 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene and 3,3,3-trichloro-1-nitropropene yields the corresponding saturated nitroalkanes in 38.6, 55, 84, 91 and 44.2% yields, respectively. Reduction of omega-nitrostyrene results in formation, along with 1-nitro-2-phenylethane, of 1,3-dinitro-2,4-diphenylbutane (tent.) as two racemates. Structures of these two racemates are based on their quantitative analyses, their chemical, physical and infrared properties and upon synthesis of one of the racemates by base-catalyzed addition of 1-nitro-2-phenylethane to omega-nitrostyrene.

Reduction of 4-nitro-3-heptene with sodium trimethoxyborohydride proceeds very slowly even at 0° and was accompanied by formation of an amine (unidentified) and a carbonyl compound (unidentified). Purification of the 4-nitroheptane may be accomplished with little difficulty, however, by distillation at reduced pressures. The relative resistance of 4-nitro-3-heptene to reduction may be attributed to possible steric factors involving the complex nitroolefin and the hindered trimethoxyborohydride ion.

The reduction of 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene and 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene occurs with rapidity and in high yields; the ease of reduction of these fluorinated nitroolefins can be associated with their relatively electron-deficient carbon-carbon double bonds. The structures of

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1,1,1,2,2,3,3-heptafluoro-5-nitrohexane and 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane were assigned on the bases of their physical constants and upon conversion to the 2,4-dinitrophenylhydrazones of 4,4,5,5,6,6,6-heptafluoro-2-hexanone and 5,5,6,6,7,7,7-heptafluoro-3-heptanone, respectively. Reduction of 3,3,3-trichloro-1-nitropropene is effected without displacement of allylic chlorine; the Michael addition product 1,1,1-trichloro-3,5-dinitro-4-trichloromethylpentane is also formed in 32.1% yield. The structures of 1,1,1-trichloro-3-nitropropane and 1,1,1-trichloro-3,5-dinitro-4-trichloromethylpentane were based on quantitative analyses and infrared spectra.

8. SELECTIVE REDUCTION OF CONJUGATED NITROOLEFINS WITH LITHIUM ALUMINUM HYDRIDE; NITROALKANES.

It has been reported recently by Gildorf and Nord¹¹ that 2-nitro-1-phenyl-1-propene and omega-nitrostyrene and by Cook, et al^{10a} that 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene and 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene may be reduced to the corresponding saturated nitro compounds with lithium aluminum hydride at -40 to -50°. The procedure used in their studies is that of addition of lithium aluminum hydride to the conjugated nitroalkanes. Since it has been found in the present studies that a successive reaction occurring in the reduction system is addition of the reduced product to unreduced nitroalkane, an investigation has been made of the reduction of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene and 3,3,3-trichloro-1-nitropropene with lithium aluminum hydride at -55°. The order of addition of reagents in the present experiments is that of conjugated nitroalkene to lithium aluminum hydride. It has been found that reduction occurs efficiently to give 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane and 1,1,1-trichloro-3-nitropropane in 85.3 and 44% yields, respectively. It is believed that the procedures of the present research are more satisfactory than those previously reported in that the competing Michael addition reactions yielding 1,3-dinitroalkanes are minimized or avoided. Additional studies of reduction of conjugated nitroalkenes with lithium aluminum hydride are in progress to illustrate the value of this method.

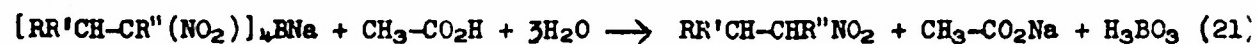
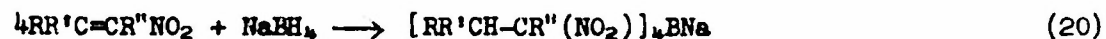
9. SELECTIVE REDUCTION OF CONJUGATED NITROOLEFINS WITH SODIUM BOROHYDRIDE; NITROALKANES.

A study has been initiated to determine the possible use of sodium borohydride for selectively reducing the carbon-carbon double bond of conjugated nitroalkenes. An attempt to reduce 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene with sodium borohydride in ethyl ether-tetrahydrofuran at -65° was unsuccessful; the initial material was recovered. It was concluded that the solubility of sodium borohydride in tetrahydrofuran-ethyl ether is not sufficient for rapid reduction to be effected. Studies have therefore been made to determine the utility of sodium borohydride in absolute ethanol as a reducing agent. It has thus been found that the carbohydrate derivative, D-arabo-

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tetraacetoxy-1-nitro-1-hexene, upon reduction with sodium borohydride at 0° in absolute ethanol, gave 1-nitro-1,2-dideoxy-D-arabo-hexitol tetraacetate in 63.9% yield upon acidification with urea-acetic acid. The general stoichiometric relations of this reduction reaction are (Equations 20 and 21):



The possible further advantageous use of sodium trimethoxyborohydride as a reducing agent for conjugated nitroolefins is being investigated.

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Experimental

1. REACTION OF 1-BROMO-1,1-DINITROETHANE AND SODIUM DIETHYL MALONATE;
FORMATION OF SODIUM 1,1-DINITROETHANE AND TETRAETHYL ETHANE-1,1,2,2-
TETRACARBOXYLATE.

A solution of sodium diethyl malonate (0.20 mole) was prepared by adding diethyl malonate (32.06 g., 0.20 mole) to sodium ethoxide (prepared from 4.60 g., 0.20 gm. atom of sodium) in absolute ethanol (220 ml.). 1-Bromo-1,1-dinitroethane (19.9 g., 0.10 mole) was then added dropwise in one hour to the cold (5-10°), stirred solution of ethanolic sodium diethyl malonate. A yellow precipitate formed almost immediately upon addition. The mixture was stirred at room temperature for 20 hours and then poured into a beaker and stirred with dry ether (400 ml.) to precipitate the insoluble sodium salts. The suspension was then filtered; the precipitate was washed with ether and dried. The initial precipitate (Ppt. I) was composed of pale-yellow salts and weighed 21.3 g. The filtrate from Ppt. I was evaporated nearly to dryness (crystals separated); addition of dry ether (300 ml.) gave a second crop of sodium salts (pale-yellow) weighing 3.7 g. (Ppt. II).

The filtrate from Ppt. II was evaporated to one-fifth its volume and then diluted with Skellysolve F (50 ml.) A pale-yellow insoluble product (Ppt. III) was obtained, and then filtered, washed with ether-Skellysolve F (1:5) and dried; the product was identified as tetraethyl ethane-1,1,2,2-tetracarboxylate (m.p. 71.5-73°); 19.8 g., 62.3% yield. Recrystallization of the tetraethyl ethane-1,1,2,2-tetracarboxylate from absolute ethanol raised its melting point to 74.5-75.5°. An authentic specimen melted at 74.5-75°; the mixed m.p. was 74.5-75.5°. The filtrate was stripped of solvents under vacuum to leave a residue weighing 10.8 g.

Anal. of Ppt. I: A 10.00 g. aliquot of Ppt. I was dissolved in water (130 ml.). Aqueous silver nitrate (17 g. in 50 ml. of water) was added to this solution. A mixture of silver salts was obtained which was filtered and washed with water (crude weight, 13.8 g.). The salts were suspended in 50% aqueous ethanol (100 ml.) and treated with 5N nitric acid (50 ml.) to dissolve the precipitated silver 1,1-dinitroethane. The remaining salt was filtered, washed with water, ethanol and ether and dried in an oven at 120° for 3 hours. Silver bromide (7.83 g.) was recovered. This corresponds to 4.29 g. of sodium bromide in the aliquot and 9.14 g. in the original salt.

A sample of Ppt. I (0.01581 g./1. 10⁻³N sodium hydroxide) was analyzed by ultraviolet methods to determine its sodium 1,1-dinitroethane content. The sodium 1,1-dinitroethane content was found to be 39.7% of the weight of sample and corresponds to 8.52 g. of sodium 1,1-dinitroethane in the original precipitate.

Anal. of Ppt. II: The mixed salts in Ppt. II were analyzed in the same manner as described for Ppt. I. The weight of sodium bromide was found to be 1.21 g.; the weight of sodium 1,1-dinitroethane was 1.15 g. In addition to these salts, 0.15 g. of impure tetraethyl ethane-1,1,2,2-tetracarboxylate (m.p. 67-68°) was isolated.

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Anal. of Residue: An aliquot (1.5813 g., 0.0131 mole if all 1,1-dinitroethane) of the residue from Pnt. III was dissolved in ethanol (8 ml.) and added to sodium hydroxide (4.0 g., 0.10 mole) in water (40 ml.) at room temperature. The solution of salts was diluted with 40% aqueous ethanol to one liter and then rediluted with water at a ratio of 1:100. The mixture was analyzed by ultraviolet methods; its E_{max} at 379-381 m μ was found to be 0.372 ($d \approx 1.00$). From this data, the residue was found to contain 17.4% or 1.88 g. of 1,1-dinitroethane.

An aliquot portion of the residue (5.00 g.) was vacuum distilled to remove the 1,1-dinitroethane and any free diethyl malonate that might be present. A fraction distilling at 59-68° (4.5-5 mm.) and weighing 1.75 g. was obtained. The infrared spectrum showed that the gem-dinitro and ester groups were present in about equal intensity. The composition was determined to be 52 mole percent diethyl malonate and 48 mole percent 1,1-dinitroethane. Thus, 1.55 g. of 1,1-dinitroethane and 2.23 g. of diethyl malonate could be isolated from the entire residue (compare the value of 1.88 g. of 1,1-dinitroethane obtained from ultraviolet analysis). The distillation residue was dissolved in absolute ethanol (ca. 2 ml.) and Skellysolve F (5 ml.) was added. Upon cooling the mixture in a Dry Ice chest and then filtering, 1.06 g. of impure tetraethyl ethane-1,1,2,2-tetracarboxylate (m.p. 46-48°) was isolated. The non-crystallizable residue (n_D^{20} 1.4402; infrared spectrum showed the presence of ester groups) weighed 2.04 g.

The reaction of 1-bromo-1,1-dinitroethane and sodium diethyl malonate is summarized: the yield of 1,1-dinitroethane (all fractions) was 77%; the combined yield of tetraethyl ethane-1,1,2,2-tetracarboxylate was 66%; the recovery of sodium bromide was 100%.

2. REACTION OF PIPERIDINE AND 1-CHLORO-1,1-DINITROETHANE; FORMATION OF PIPERIDINIUM 1,1-DINITROETHANE AND PIPERIDINIUM CHLORIDE.

1-Chloro-1,1-dinitroethane (15.5 g., 0.10 mole) was added rapidly to a solution of piperidine (17.0 g., 0.20 mole) in anhydrous ether (100 ml.). The resulting pale-yellow solution was shaken, then allowed to stand at room temperature. After one hour, fine needles began to precipitate; after two days, an oil began separating. The oily precipitate was filtered and washed with ether containing a small amount of ethanol (to dissolve the oil); the filtrate and washings (I) were combined and saved. The golden-yellow precipitate, after being dried in a desiccator over calcium sulfate for 2 days, weighed 7.3 g.

The yellow precipitate of salts was analyzed by ultraviolet methods and found to contain 58.5% (or 4.27 g.) of piperidinium 1,1-dinitroethane. The mixture of precipitated salts was then analyzed for piperidinium chloride in the following manner: A 5.00 g. aliquot of the salt was treated with excess silver nitrate; the mixture of silver salts formed was acidified with nitric acid in aqueous ethanol in order to dissolve the precipitated silver 1,1-dinitroethane. The silver chloride left, upon being filtered and dried, weighed 1.14 g. The silver chloride isolated is equivalent to 1.40 g. of piperidinium chloride in the original precipitate of salts.

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The filtrate (I) was allowed to stand at room temperature for another day; no further precipitation of salt was observed. The filtrate was concentrated at reduced pressure; a residual oil remained which contained some crystals and weighed 21.2 g. The residue was extracted with a mixture of water and ether; the aqueous extract was then diluted with water to a stock volume of 1000 ml. The solution was then rediluted, 1:1000, and analyzed spectrophotometrically. Ultra-violet analysis of the rediluted mixture indicated that the stock solution contained piperidinium 1,1-dinitroethane in 0.0245 M concentration (equivalent to 5.01 g.). The remainder of the stock solution was treated with silver nitrate (as outlined above), and 0.96 g. of silver chloride was obtained. The silver chloride isolated is equivalent to 0.81 g. of piperidinium chloride.

The ether extract (from the residual oil), after removal of the solvent, was vacuum distilled. The forerun was lachrymatory 1-chloro-1,1-dinitroethane (1.0 g.), b.p. 58-61° (22 mm.). The distillates: Fractions 2 (1.92 g., b.p. 72-85° (3 mm.), n_D^{20} 1.4840) and 3 (2.98 g., b.p. 85-88° (3 mm.), n_D^{20} 1.4891), and the residue (3.0 g.) were not identified further.

The products of reaction of 1-chloro-1,1-dinitroethane and piperidine are summarized: piperidinium 1,1-dinitroethane (9.28 g., 48.6% yield), piperidinium chloride (2.21 g., 20.6% yield), 1-chloro-1,1-dinitroethane (1.0 g., 6.45% recovery), unidentified distillate (4.90 g.) and unidentified residue (3.0 g.). The total weight of isolated products is 20.4 g., theory 32.5 g.; the material balance is 62.8%.

3. REACTION OF SILVER 1,1-DINITROETHANE AND o-NITROBENZENESULFENYL CHLORIDE; o-NITROPHENYL 1,1-DINITROETHYL SULFIDE.

A solution of silver 1,1-dinitroethane (27.4 g., 0.099 mole) in acetonitrile (150 ml.) was added in 45 minutes to o-nitrobenzenesulfonyl chloride (19.0 g., 0.10 mole) stirred in acetonitrile (150 ml.) at 10°. Heat was evolved (the temperature rose slowly to ca. 30°) and silver chloride immediately precipitated. After the mixture had stirred for 10 hours, the silver chloride was filtered, washed with acetonitrile and dried at 120° for three hours; recovery = 12.6 g. (theoretical yield, 14.19 g.). The filtrate was evaporated at reduced pressure to dryness. The crude, sweet-smelling, oily, tan solid that was isolated weighed 26.4 g. The solid was alternately dried on filter paper and ground in a mortar to express and adsorb the oil. The dry, tan solid remaining weighed 22.9 g.; in a closed capillary, it began melting at 75° and decomposed rapidly at 140-145°. The derivative is insoluble in water, dilute acid and dilute alkali; slightly soluble in ether and cold 95% ethanol; soluble in hot 95% ethanol, carbon tetrachloride, benzene, acetone, acetonitrile and glacial acetic acid.

Recrystallization of the derivative (2.00 g.) from 95% ethanol (14 ml.) gave pure o-nitrophenyl 1,1-dinitroethyl sulfide (1.47 g.) as cream-colored needles, m.p. 80.0-81.0°. Evaporation of the filtrate gave additional

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o-nitrophenyl 1,1-dinitroethyl sulfide (0.27 g., impure).

Anal. Calcd. for $C_8H_7N_2SO_3$: C, 35.17; H, 2.58; N, 15.38; S, 11.78.
Found: C, 34.79; H, 3.00; N, 15.34; S, 11.72.

4. REACTION OF SILVER 1,1-DINITROPROPANE AND *o*-NITROBENZENESULFONYL CHLORIDE;
o-NITROPHENYL 1,1-DINITRO-*n*-PROPYL SULFIDE.

Silver 1,1-dinitropropane (24.1 g., 0.10 mole) in acetonitrile (150 ml.) was added in 45 minutes to a stirred solution of *o*-nitrobenzenesulfonyl chloride (19.0 g., 0.10 mole) in acetonitrile (180 ml.) at 20°. Silver chloride immediately precipitated from the solution. After stirring the suspension at 25° for 4 hours, the salt was filtered, washed with acetonitrile and ether, then dried in an oven at 90° for 5 hours. The recovery of silver chloride was 14.36 g. (theoretical yield = 14.33 g.). The filtrate was evaporated at reduced pressure to dryness. The crude, crystalline residue weighed 29.0 g.; four days of drying on filter paper brought its weight down to 28.6 g. The theoretical yield of *o*-nitrophenyl 1,1-dinitro-*n*-propyl sulfide is 28.7 g. Recrystallization of the derivative (21.9 g.) from 95% ethanol (160 ml.) gave *o*-nitrophenyl 1,1-dinitro-*n*-propyl sulfide (17.25 g.) as cream-colored needles, m.p. 90.5-91.5°.

Anal. Calcd. for $C_9H_9N_2SO_3$: C, 37.63; H, 3.16; N, 14.63; S, 11.16.
Found: C, 37.75; H, 3.27; N, 14.62; S, 11.17.

5. REACTION OF 2-NITRO-1-BUTENE AND METHANOL; 1-METHOXY-2-NITROBUTANE.

2-Nitro-1-butene (25 g., 0.25 mole) was added over a period of 45 minutes to a stirred solution of sodium methoxide in methanol (5.75 g., 0.25 mole of sodium in 125 ml. of methanol) at room temperature. Stirring was continued for 3 hours following the complete addition of the nitroolefin. The solution was diluted with water (250 ml.), neutralized with 30% acetic acid, and extracted 4 times with ether. These extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was distilled; 1-methoxy-2-nitrobutane (18.9 g.) was produced in 57% crude yield (b.p. 79.8-83.0° (12 mm.)). Redistillation in a small column gave a 48% yield of pure 1-methoxy-2-nitrobutane (b.p. 75.2° (11 mm.), n_D^{20} 1.4201, d_4^{20} 1.0372).

Anal. Calcd. for $C_5H_{11}NO_3$: C, 45.11; H, 8.27; N, 10.52.
Found: C, 45.31; H, 8.41; N, 10.30.

The infrared spectrum of the pure product indicates absorption for mononitro (6.4 microns) and ether (9.0 microns) groups.

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6. OXIDATIVE-NITRATION OF 1-METHOXY-2-NITROBUTANE; 1-METHOXY-2,2-DINITROBUTANE.

1-Methoxy-2-nitrobutane (6.65 g., 0.05 mole) was dissolved in a cold solution of sodium hydroxide (2.1 g., 0.052 mole) and sodium nitrite (3.7 g., 0.05 mole, 97% assay) in water (30 ml.) and methanol (50 ml.). This solution was poured directly into aqueous silver nitrate (17.0 g., 0.1 mole in 50 ml. of water) which had been cooled to 0°. After stirring for 2 hours, aqueous sodium chloride (10 ml.) was added. The precipitate was filtered and washed with ether. The layers in the filtrate were separated, and the water layer was washed 3 times with ether. The extracts were combined with the ether layer, washed with saturated sodium chloride solution, and dried over Drierite. Solvent was removed and the residue was distilled. A crude yield of 87% of 1-methoxy-2,2-dinitrobutane (b.p. 60.5-62.5°/1.5 mm., 7.75 g.) was obtained. Redistillation of the crude material gave pure 1-methoxy-2,2-dinitrobutane (b.p. 67.2°/(3 mm.), 5.44 g., n_D^{20} 1.4345, d_4^{20} 1.2107, 61%).

Anal. Calcd. for $C_5H_{10}N_2O_5$: C, 33.71; H, 5.62; N, 15.75; MR_D , 38.38.
Found: C, 33.70, 33.80; H, 5.69, 5.55;
N, 15.71, 15.72; MR_D , 38.33.

The infrared spectra of the product exhibits characteristic absorption for gem-dinitro (6.3 microns) and ether (9.0 microns) groups.

7. REACTION OF ANILINE AND 2-NITRO-1-BUTENE; 2-NITRO-1-PHENYLAMINO BUTANE.

Aniline (22.0 g., 0.237 mole) was added dropwise to well-stirred 2-nitro-1-butene (25.0 g., 0.25 mole) at temperatures below 30°. A solution of the resulting yellow solid in dry ether (250 ml.) was then dropped into cold ethereal hydrogen chloride (250 ml.). The amine hydrochloride that precipitated was triturated twice with methanol-ether (1:2) and filtered. A crude yield of 67 g. of 2-nitro-1-phenylaminobutane hydrochloride was obtained, m.p. 131-135°.

The hydrochloride was dissolved in water (500 ml.) and converted to the free amine by the addition of dilute sodium carbonate. The basic solution was extracted 3 times with ether. The extracts were combined, dried over sodium sulfate, and concentrated under reduced pressure. Upon distillation under nitrogen atmosphere, the residue gave crude 2-nitro-1-phenylaminobutane (35.8 g., b.p. 134-137°(1.5 mm.), 78% yield) as a yellow oil. Redistillation of the product yielded pure 2-nitro-1-phenylaminobutane: b.p. 121°(0.1 mm.), n_D^{20} 1.5467, d_4^{20} 1.1128, yield of 70%.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.86; H, 7.22; N, 14.44; MR_D 55.67.
Found: C, 62.15; H, 7.27; N, 14.81; MR_D 55.26.

Infrared analysis of the product shows the presence of amine (2.95 and 6.16 microns), mononitro (6.4 microns) and phenyl (13.25 and 14.5 microns) groups.

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8. OXIDATIVE-NITRATION OF 2-NITRO-1-PHENYLAMINO BUTANE; 2,2-DINITRO-1-PHENYLAMINO BUTANE.

2-Nitro-1-phenylaminobutane (4.65 g., 0.025 mole) was dissolved in a cold solution of sodium hydroxide (1.12 g., 0.028 mole) and sodium nitrite (1.72 g., 0.025 mole) in water (30 ml.) and methanol (50 ml.). The mixture was poured directly into cold aqueous silver nitrate solution (6.5 g., 0.05 mole in 50 ml. of water and 100 ml. of ether). After the mixture had stirred for 3 hours, brine (20 ml.) was added, and the solution was filtered. The silver precipitate was washed with ether. The aqueous layer in the filtrate was separated and washed 3 times with ether. The extracts and the ether layer were combined, washed with saturated sodium chloride solution and dried over Drierite. A dark oil remained after the solvent had been distilled off under reduced pressure. The oil was decolorized with charcoal and added immediately to ethereal hydrogen chloride (250 ml.) at 0°. The nearly-white precipitate was filtered and dried, yielding the hydrochloride of 2,2-dinitro-1-phenylaminobutane (3.21 g., m.p. 72-73°, 45%). This product decomposes to a dark oil unless it is refrigerated.

Anal. Calcd. for $C_{10}H_{14}N_3O_4Cl$: C, 43.64; H, 5.10; N, 15.28.
Found: C, 43.64, 43.69; H, 5.37, 5.20;
N, 15.20, 15.43.

9. REACTION OF 2-NITRO-1-BUTENE AND ETHANETHIOL; ETHYL 2-NITRO-1-BUTYL THIOETHER.

Sodium methoxide (5.75 g., 0.25 mole of sodium in 100 ml. of methanol) was added slowly with stirring to a solution of ethanethiol (24 g., 0.39 mole) in methanol (60 ml.) at -5°. 2-Nitro-1-butene (25 g., 0.25 mole) was then added over a period of 45 minutes. After an hour of stirring at -5°, the solution was diluted with water (400 ml.) and acidified with 30% acetic acid. The thioether was extracted with ether and dried over anhydrous sodium sulfate. Removal of the solvent and distillation of the residue produced a yellow oil (34.1 g., b.p. 87.5-90.0° (12 mm.), 84%). Redistillation on a small column gave pure ethyl 2-nitro-1-butyl thioether (b.p. 83.0° (3 mm.), 30.60 g., n_D^{20} 1.4752, d_4^{20} 1.0642, 75%; MR_D calcd: 43.21, found: 43.14). The infrared spectra of the product exhibits absorption characteristics of mononitro (6.4 microns) and thioether (9.0 and 11.85 microns) groups.

Anal. Calcd. for $C_6H_{13}NO_2S$: C, 44.17; H, 7.98; N, 8.59.
Found: C, 44.36, 44.31; H, 8.11, 8.17;
N, 8.44, 8.52.

10. OXIDATIVE-NITRATION OF ETHYL 2-NITRO-1-BUTYL THIOETHER; ATTEMPTED PREPARATION OF ETHYL 2,2-DINITRO-1-BUTYL THIOETHER.

2-Nitro-1-butyl thioether (4.17 g., 0.0256 mole) was dropped slowly into a cold solution of sodium hydroxide (1.10 g., 0.025 mole) and sodium nitrite (1.90 g., 0.027 mole, 97% assay) in water (30 ml.) and methanol (20 ml.). Vigorous shaking of the mixture for several minutes was required before the nitrothioether was completely dissolved. The solution was then

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poured directly into aqueous silver nitrate (8.50 g., 0.05 mole in water (50 ml.) and ether (100 ml.) at 0°. A black silver precipitate formed immediately. The reaction mixture now exhibited a strong lachrymatory odor. Upon stirring the reaction mixture for 3 hours, no apparent changes could be observed. Brine (10 ml.) was added and the solution was filtered. The precipitate was washed with hot benzene (2 x 10 ml.) and ether (3 x 20 ml.). The aqueous layer in the filtrate was separated and extracted 3 times with ether. The extracts were combined with the ether layer, washed with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure and distillation of the residue yielded 0.54 g. of a yellow oil (67-85°/0.8 mm.). Infrared analysis indicated that this material was a mixture of mononitro (6.4 μ) and dinitro (6.3 μ) thioethers.

It was concluded from this experiment that the principal portion of the starting material was converted to 2-nitro-1-butene, apparently at the moment of contact with the silver nitrate solution. Although the salt of ethyl 2-nitro-1-butyl thioether seemed entirely stable, a critical factor was found in its preparation. If the salt of the mononitro compound was not dissolved in a minimum of solvent (water-alcohol) and used within a half-hour or so, after its preparation, no black precipitate was formed upon addition of sodium nitrite-silver nitrate reagents.

11. OXIDATIVE-NITRATION OF 4-NITROPENTANAL; 4,4-DINITROPENTANAL.

4-Nitropentanal (5.32 g., 0.041 mole, b.p. 84-88° (2.5 mm.)), in 75 ml. of methanol) was dissolved in aqueous sodium hydroxide (1.64 g., 0.041 mole, in 10 ml. water) at 0° (15 minutes). Sodium nitrite (2.83 g., 0.041 mole, 97% assay, in 10 ml. of water) was added and the solution was poured into stirred aqueous silver nitrate (13.94 g., 0.082 mole, in 100 ml. of water) and ether (75 ml.) at 0-5°. Silver was deposited very slowly. After one hour at 0°, the reaction mixture was brought to room temperature for one hour. The mixture was filtered and extracted with ether. The ether extracts were washed with saturated sodium chloride and then with water and dried with Drierite. Distillation of the reaction mixture gave 4,4-dinitropentanal (4.43 g., 61.6% theory, b.p. 123-124.5° (4 mm.)), n_D^{20} 1.4675, d_4^{20} 1.3253; lit.² b.p. 97-97.5° (0.8 mm.), d_{20}^{20} 1.3284, n_D^{20} 1.4650, MR_D (calcd.) 36.65, MR_D (found) 36.65).

4,4-Dinitropentanal was characterized as its semicarbazone (m.p. 153.5-154.5°; lit.¹² m.p. 154.5-155.5°) and its p-nitrophenylhydrazone (m.p. 142-143°; lit.¹² m.p. 141-142°).

12. OXIDATIVE-NITRATION OF 1,1,1,2,2,3,3-HEPTAFLUORO-5-NITROHEPTANE;
1,1,1,2,2,3,3-HEPTAFLUORO-5,5-DINITROHEPTANE.

1,1,1,2,2,3,3-Heptafluoro-5-nitroheptane (4.73 g., 0.017 mole) in methanol (50 ml.) was slowly mixed with aqueous sodium hydroxide (0.72 g., 0.018 mole, in 20 ml. of water) at 10° and the solution was allowed to stand for 10 minutes. Sodium nitrite (1.25 g., 0.018 mole) was added and the

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cooled solution was poured into stirred silver nitrate (6.12 g., 0.036 mole) in water (75 ml.) and ether (100 ml.) at 5°. After 30 minutes the cooling bath was removed and the reaction mixture was stirred at room temperature for 2 hours. Brine (5 ml.) was added, and the mixture was filtered by suction. The silver deposit was washed liberally with ether, and the aqueous layer was extracted several times with ether. The combined ether washings and extracts were washed with water, brine and dried over Drierite. After ether had been distilled, the crude product was distilled at reduced pressure, giving 1,1,1,2,2,3,3-heptafluoro-5,5-dinitroheptane: Fraction 1, 0.68 g., b.p. 48-52° (2 mm.), n_D^{20} 1.3648, Fraction 2, 3.34 g., b.p. 52-53° (2 mm.), n_D^{30} 1.3660, total yield, 4.02 g., 74.9% theory. Redistilled 1,1,1,2,2,3,3-heptafluoro-5,5-dinitroheptane has the following physical properties: b.p. 73° (9 mm.), n_D^{20} 1.3708, d_4^{20} 1.5382, MR_D (calcd.) 46.46, MR_D (found) 46.58. Infrared analysis of the heptafluorodinitroalkane showed the dinitro absorption band at 6.25 microns instead of the usual 6.3 microns for gem-dinitroalkanes.

Anal. Calcd. for $C_7H_7F_7N_2O_4$: C, 26.59; H, 2.23; N, 8.86.

Found: C, 26.85; H, 2.34; N, 8.97.

13. REACTION OF 1-BROMO-2-PHENYLETHANE AND SILVER NITRITE; 1-NITRO-2-PHENYLETHANE.

Silver nitrite (40 g., 0.26 mole) was introduced into a one liter, round-bottomed flask, equipped with a condenser, a stirrer and a dropping funnel. The mixture was cooled to 0° and 1-bromo-2-phenylethane (31.59 g., 0.17 mole) was added dropwise in one hour. The reaction mixture was stirred at 0° for 5 hours and then left to stir overnight at room temperature. After heating the mixture for 5 hours on a steam bath, ethyl ether (150 ml.) was added and the silver bromide was filtered by suction. Vacuum distillation of the solution gave the following fractions: Fraction 1, 3.35 g., b.p. 45-55° (1.5 mm.), d_{20}^{20} 1.0638; Fraction 2, 2.10 g., b.p. 65-70° (1.5 mm.), d_{20}^{20} 1.0680; Fraction 3, 3.45 g., b.p. 70-77° (1.5 mm.), d_{20}^{20} 1.0837; Fraction 4, 12.00 g., b.p. 77-85° (1.5 mm.), d_{20}^{20} 1.1354. Rectification of Fraction 4 in a helix-packed column (1.5 x 13 cm.) gave 1-nitro-2-phenylethane 11.25 g., 43.8% yield, b.p. 88-89° (2 mm.), n_D^{22} 1.5258, d_{20}^{20} 1.1239; MR_D (calcd.) 41.37, MR_D (found) 41.27; lit.¹³ b.p. 74.5-75.5° (0.5 mm.), n_D^{20} 1.5273, d_{20}^{20} 1.1225.

14. OXIDATIVE-NITRATION OF 1-NITRO-2-PHENYLETHANE; 1,1-DINITRO-2-PHENYLETHANE.

1-Nitro-2-phenylethane (5.54 g., 0.037 mole, b.p. 88-89° (3 mm.), d_{20}^{20} 1.1239) in methanol (40 ml.) was added slowly to aqueous sodium hydroxide (1.52 g., 0.038 mole) in 20 ml. of water; the solution was allowed to stand for one half hour below 10°. Sodium nitrite (2.62 g., 0.038 mole) in 10 ml. of water was added and the mixture was cooled in an ice-bath. The yellow solution was poured rapidly into a stirred solution of silver nitrate (11.92 g., 0.076 mole) in water (100 ml.) and ethyl ether (100 ml.) at 0°.

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After 30 minutes the cooling bath was removed and the reaction mixture was stirred at room temperature for 2 hours. The deposition of silver during oxidative-nitration was very rapid. Brine (5 ml.) was added; the mixture was filtered by suction. The silver deposit was washed liberally with ether. The ether extracts were combined, washed with saturated sodium chloride solution and water, dried with Drierite, filtered, and then evaporated. A crystalline residue remained which upon recrystallization from petroleum ether gave 1,1-dinitro-2-phenylethane 3.97 g., 54.7% yield, m.p. 41-42°, infrared absorption for gem-dinitro group at 6.3 microns.

Anal. Calcd. for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28.
Found: C, 49.21; H, 3.81; N, 14.30.

Potassium 1,1-dinitro-2-phenylethane (0.626 g., 0.0022 mole, 87.7% theory) was obtained as a yellow salt by treating 1,1-dinitro-2-phenylethane (0.598 g., 0.0031 mole) in methanol (10 ml.) with methanolic potassium hydroxide. The precipitated potassium salt was filtered, washed several times with ethyl ether, dec. range, 143-150°. Solubility of potassium 1,1-dinitro-2-phenylethane in water, 1 part to 7.01 parts water.

Silver 1,1-dinitro-2-phenylethane was obtained as a water-insoluble grayish yellow solid (0.435 g., 0.0014 mole, 92.0% theory) on mixing aqueous solution of potassium 1,1-dinitro-2-phenylethane (0.365 g., 0.016 mole) and silver nitrate; dec. range, 140-146°, at which silver salt began to deposit silver mirror.

15. OXIDATIVE-NITRATION OF NITROCYCLOPENTANE; DINITROCYCLOPENTANE.

Nitrocyclopentane (7.22 g., 0.063 mole) in methanol (100 ml.) was slowly mixed with aqueous sodium hydroxide (2.6 g., 0.065 mole, in 15 ml. water) and the solution was allowed to stand for 15 minutes below 15°. Sodium nitrite (4.5 g., 0.065 mole, in 15 ml. of water) was added and the mixture was cooled in an ice-bath and poured into stirred silver nitrate (22.10 g., 0.13 mole, in 100 ml. of water), aqueous sodium hydroxide (5%, 1 drop), and ether (100 ml.). After 30 minutes the cooling bath was removed and left stirring for an additional 4 hours. Silver deposition was very slow; brine (5 ml.) was added and the mixture filtered by suction. The combined ether washings were washed with saturated sodium chloride, with water and dried with Drierite. Distillation under reduced pressure gave dinitrocyclopentane (5.63 g., 55.8% theory, b.p. 78° (2 mm.), n_D^{30} 1.4655, d_4^{20} 1.2809). Rectification of the dinitrocyclopentane in a helix-packed column (1.5 x 13 cm.) gave a product of the following properties: b.p. 80° (2 mm.), n_D^{22} 1.4668, d_4^{20} 1.2818, MR_D (calcd.) 34.605, MR_D (found) 34.65.

Anal. Calcd. for $C_5H_8N_2O_4$: C, 37.50; H, 5.04; N, 17.49.
Found: C, 37.80; H, 5.17; N, 17.14.

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16. OXIDATIVE-NITRATION OF 2,2-DIMETHYL-1-NITROPROPANE; 2,2-DIMETHYL-1,1-DINITROPROPANE (IMPROVED YIELD).

2-Methyl-1-nitropropane (9.56 g., 0.081 mole) in methanol (50 ml.) was added to aqueous sodium hydroxide (4.2 g., 0.11 mole, in 20 ml. water) at 0°. Sodium nitrite (7.5 g., 0.11 mole, 97% assay) was added and the solution was poured into stirred aqueous silver nitrate (34.0 g., 0.20 mole, in 150 ml. water) and ether (100 ml.) at 0-5°. Silver deposits were formed rather rapidly. After one hour brine (5 ml.) was added; the mixture was left overnight since it was difficult to filter the finely divided silver precipitate. The mixture was filtered through a layer of Celite and washed with additional ether. The combined ether extracts were dried with Drierite and evaporated, leaving an oily mass which was purified by recrystallization from Skellysolve F, followed by sublimation to give 2,2-dimethyl-1,1-dinitropropane (7.35 g., 55.5% theory, m.p. 64-65°; lit., 45 m.p. 64.5-65°).

17. OXIDATIVE-NITRATION OF CYCLOHEXYLNITROMETHANE; CYCLOHEXYLDINITROMETHANE (IMPROVED YIELD).

Cyclohexylnitromethane (5.20 g., 0.036 mole, n_D^{20} 1.4635, d_4^{20} 1.0405; obtained from Dr. N. Kornblum) in methanol (70 ml.) was slowly added to aqueous sodium hydroxide (1.52 g., 0.038 mole, 97% assay, in 15 ml. water) and the solution allowed to stand for half an hour below 15°. Sodium nitrite (2.62 g., 0.038 mole, 97% assay, in 7 ml. of water) was added and the mixture was cooled in an ice-bath and poured rapidly into a stirred solution of silver nitrate (12.9 g., 0.076 mole, in 50 ml. water) and ether (75 ml.) at 0°. After 30 minutes the cooling bath was removed; brine (5 ml.) was added, and the mixture was filtered by suction. The silver deposit was washed repeatedly with ether; the ether layer in the filtrate was separated and the aqueous layer was washed with ether. The ether washings were combined, washed with brine, water, and dried with Drierite. Distillation under reduced pressure gave cyclohexyldinitromethane (4.72 g., 69.7% yield), b.p. 94° (2 mm.), n_D^{20} 1.4767, d_4^{20} 1.2129, M_p (calcd.) 44.79, M_p (found) 43.82.

Anal. Calcd. for C₇H₁₂N₂O₄: C, 44.67; H, 6.43; N, 14.89.

Found: C, 44.87, 44.93; H, 6.69, 6.45;
N, 14.82, 14.98.

18. REACTION OF SILVER NITRITE AND ETHYL 3-BROMOBUTYRATE; ETHYL 3-NITROBUTYRATE.

Silver nitrite (61.6 g., 0.40 mole) was introduced into a one liter, round bottomed flask, equipped with a condenser, a stirrer and a dropping funnel. The flask was cooled to 0° and ethyl 3-bromobutyrate (60 g., 0.31 mole, b.p. 57-68° (6 mm.), n_D^{25} 1.4472, d_4^{20} 1.3366, Sapon Laboratories, Inc.) was added dropwise in one hour. The mixture was then stirred at 0° for 4 hours. The mixture was left overnight at room temperature and then heated at 70° for

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7 hours. Ethyl ether (150 ml.) was added and the silver bromide was filtered by suction. Vacuum distillation of the reaction mixture gave the following fractions: Fraction 1, 14.2 g., b.p. 52-58° (3 mm.), n_D^{29} 1.4168, d_{20}^{20} 1.0584, Fraction 2, 13.8 g., b.p. 60-70° (3 mm.), n_D^{29} 1.4205, d_{20}^{20} 1.1400, Fraction 3, 7.7 g., b.p. 70-77° (3 mm.), n_D^{29} 1.1408, d_{20}^{20} 1.1408, Fraction 4, 6.5 g., pot residue. Fraction 3 was rectified in a helix-packed column (1.5 x 13 cm.) to yield ethyl 3-nitrobutyrate, 7.2 g., 14% yield, b.p. 72-73° (2 mm.), n_D^{25} 1.4241, d_{20}^{20} 1.1408, MR_D (calcd.) 37.13, MR_D (found) 36.06. Infrared analysis of the product showed the usual mononitro absorption at 6.4 microns, and strong nitrate absorption at 6.1 microns.

Anal. Calcd. for $C_6H_{11}NO_4$: C, 44.71; H, 6.88; N, 8.69.
Found: C, 44.46; H, 6.65; N, 8.49.

Fraction 2 (13.8 g., b.p. 60-70° (3 mm.), n_D^{29} 1.4205, d_{20}^{20} 1.1400) was also rectified in a helix-packed column (1.5 x 13 cm.) to yield nearly pure ethyl 3-nitrobutyrate (5.6 g., 11% yield, b.p. 69-70° (2 mm.), n_D^{25} 1.4236, d_{20}^{20} 1.138). Infrared analyses of all fractions indicated always the presence of nitrate (6.1 microns) groups.

19. OXIDATIVE-NITRATION OF ETHYL 3-NITROBUTYRATE: ETHYL 3,3-DINITROBUTYRATE.

Ethyl 3-nitrobutyrate (4.95 g., 0.032 mole) in methanol (35 ml.) was slowly mixed with aqueous sodium hydroxide (1.4 g., 0.035 mole, in 15 ml. of water) and the solution was allowed to stand for 15 minutes below 15°. Sodium nitrite (2.4 g., 0.035 mole) in 10 ml. of water was then added. The mixture was cooled in an ice-bath and poured into stirred silver nitrate (11.9 g., 0.07 mole) in water (110 ml.) and ether (100 ml.) at 5°. After 30 minutes the cooling bath was removed. The color of the reaction mixture changed from cream to light brown to dark brown to black with silver deposits on the sides of the flask within the course of 15 minutes. Brine (5 ml.) was added, and the mixture was filtered by suction. After the silver deposit had been washed liberally with ether, the aqueous layer was extracted with ether. The combined ether washings and extracts were washed with water, brine and dried over Drierite. After the ether had been distilled, the crude product was distilled at reduced pressure to give ethyl 3,3-dinitrobutyrate, 2.28 g., 35.7% theory, b.p. 67° (0.5 mm.), n_D^{22} 1.4485. The infrared spectrum of the product exhibited absorption at 6.3 microns characteristic of the gem-dinitro group.

Anal. Calcd. for $C_6H_{10}N_2O_6$: C, 34.95; H, 4.89; N, 13.59.
Found: C, 35.20; H, 5.13; N, 13.89.

20. CONDENSATION OF NITROMETHANE AND FLUORAL HYDRATE; 1,1,1-TRIFLUORO-3-NITRO-2-PROPANOL (IMPROVED PROCEDURE).

Procedure 1. A mixture of fluoral hydrate (76 g. of fluoral hydrate-water azeotrope, 56 g. hydrate, 0.48 mole), nitromethane (92 g., 1.5 mole),

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and dry sodium carbonate was stirred for 2 days at room temperature. The mixture was washed with water to remove any remaining base; the aqueous extracts were then extracted with ether. The combined oil and ether fractions were dried over Drierite; the ether and nitromethane were removed by distillation at 50 mm. The residual oil was distilled at reduced pressure to give colorless 1,1,1-trifluoro-3-nitro-2-propanol (62.36 g., 81% yield), b.p. 62-66° (5.5 mm.), n_D^{20} 1.3791; lit.¹⁰ n_D^{20} 1.3771, 47% yield.

Procedure 2. The procedure followed was the same as that previously described with the exception that the solution was heated at 50° for 4 hours and allowed to stand overnight. The yield of 1,1,1-trifluoro-3-nitro-2-propanol was essentially the same as that of the previous procedure (64.43 g., 83% yield) b.p. 62-66° (5.5 mm.), n_D^{20} 1.3792; lit.¹⁰ n_D^{20} 1.3771.

21. REACTION OF 1,1,1-TRIFLUORO-3-NITRO-2-PROPYL ACETATE AND SODIUM CARBONATE; ATTEMPTED PREPARATION OF 3,3,3-TRIFLUORO-1-NITRO-1-PROPENE.

Acetic anhydride (41 g., 0.4 mole) was added dropwise to a stirred mixture of 1,1,1-trifluoro-3-nitro-2-propanol (64 g., 0.4 mole) and concentrated sulfuric acid (0.5 g.). The solution was heated at 80-90° for 6 hours and then cooled and poured into water (500 ml.). The mixture was allowed to stand for one hour and then extracted with ether; the ether extracts were then dried over Drierite. The ether solution was concentrated to a volume of 150 ml., and dry sodium carbonate (42 g., 0.4 mole) was added. The mixture darkened in color upon being warmed and heat was evolved. After filtering the mixture the precipitated cake was dissolved in water and extracted with ether. The ether fractions were combined, dried over Drierite, and then distilled. Distillation of the lachrymatory residual oil gave a mobile mixture (19.4 g., b.p. 55-110°) which could not be effectively separated by rectification in a small packed column; a viscous dark tar (14.3 g.) remained as a residue (unidentified) from the initial distillation. (It has been previously reported¹⁰ that the reaction product obtained from phosphoric anhydride and 1,1,1-trifluoro-3-nitro-2-propanol could not be separated in a 50 plate column).

22. REACTION OF 1,1,1-TRIFLUORO-3-NITRO-2-PROPANOL AND PHTHALIC ANHYDRIDE; 3,3,3-TRIFLUORO-1-NITRO-1-PROPENE.

A mixture of 1,1,1-trifluoro-3-nitro-2-propanol (45.5 g., 0.286 mole) and phthalic anhydride (45.5 g., 0.30 mole) was heated at 140° until it became homogeneous in an apparatus equipped for vacuum distillation. The temperature of the mixture was raised to 180° and the product mixture of oil and water was collected. The pressure in the apparatus was gradually lowered during the dehydration until no more volatile product was being formed. The distillate was dissolved in ether and the water separated; the ether solution was distilled through a small column. The reaction product was isolated in the following fractions: Fraction 1, b.p. 86-87°, 4.62 g., n_D^{20} 1.3605; Fraction 2, b.p. 87-89°, 11.37 g., n_D^{20} 1.3609, Fraction 3,

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89-89.5°, 3.21 g., n_D^{20} 1.3610. The product, 3,3,3-trifluoro-1-nitropropane, (19.20 g., 47% yield, n_D^{20} 1.3609, d_{20}^{20} 1.423) was a very strong lachrymator.

Anal. Calcd. for $C_3H_2F_3NO_2$: C, 25.53; H, 1.42; N, 9.93.
Found: C, 26.33; H, 1.71; N, 10.25.

23. CONDENSATION OF NITROMETHANE AND 1,1,1-TRIFLUOROACETONE; 1-NITRO-2-TRIFLUOROMETHYL-2-PROPANOL.

1,1,1-Trifluoroacetone (25.0 ml., 30.1 g., 0.269 mole) was added dropwise with stirring to nitromethane (500 ml., 565 g., 9.2 mole) at 0° containing anhydrous potassium carbonate (4.0 g.). The solution was allowed to warm to room temperature and stir for 3 days. After being neutralized with dilute hydrochloric acid, the mixture was dried first with a saturated salt solution and then with sodium sulphate. After the nitromethane had been removed at reduced pressure, the residual oil was vacuum distilled twice to give colorless 1-nitro-2-trifluoromethyl-2-propanol (24.53 g., 53% yield), b.p. 42-43° (3 mm.), n_D^{20} 1.3881, d_{20}^{20} 1.2302.

Anal. Calcd. for $C_4H_6F_3NO_3$: C, 27.75; H, 3.49; N, 8.09.
Found: C, 27.96; H, 3.32; N, 8.04.

24. REDUCTION OF 1-NITROPROPENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 1-NITROPROPANE, 2-METHYL-1,3-DINITROPENTANE (COMPLETED EXPERIMENT).

A solution of 1-nitropropene (15.2 g., 0.175 mole) in ethyl ether (25 ml.) was added dropwise in 70 minutes to a stirred suspension of sodium trimethoxyborohydride (33.58 g., 0.175 mole + 50% excess) in ethyl ether (150 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at $-70^\circ \pm 1^\circ$; after addition was completed the mixture was stirred for 30 minutes at -72° . The mixture was then acidified in 1 hour at 0° with urea-acetic acid solution (100 ml.). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration, distillation gave, after removal of ether, the following fractions: (1) 1-nitropropane (12.73 g., 0.143 mole, 81.7%) as a colorless liquid, b.p. 40-72° (100 mm.), n_D^{20} 1.4025-1.4046, d_{20}^{20} 1.0006; MR_D (calcd.) 21.68, MR_D (found) 21.96, and (2) 2-methyl-1,3-dinitropentane (1.75 g., 0.00994 mole, 11.4%) as a yellow-liquid, b.p. 105-108.5° (2 mm.), n_D^{20} 1.4563, and (3) a residue (0.9 g.).

Redistillation of Fraction 1 gave purer 1-nitropropane in slightly lower yield, b.p. 128-130°, n_D^{20} 1.4027; lit.¹⁴ b.p. 132, d_{20}^{20} 1.003, n_D^{20} 1.4015. An infrared spectrum of the 1-nitropropane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a mononitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

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The structure of 1-nitropropane was proven by its conversion to propionaldehyde via the Nef reaction¹⁶ followed by preparation of propionaldehyde 2,4-dinitrophenylhydrazone, m.p. 153-155°. The melting point of the derivative was not depressed when mixed with an authentic sample.

Fraction 2, crude 2-methyl-1,3-dinitropentane, was redistilled twice to give a colorless product in only slightly lower yield, b.p. 86-86.80 (0.8 mm.), n_D^{20} 1.4558, d_4^{20} 1.1707; MR_D (calcd.) 41.31, MR (found) 40.89. Its infrared spectrum indicated the presence of aliphatic mononitro groups (C-NO₂ at 6.4 microns). The following analysis was obtained for 2-methyl-1,3-dinitropentane:

Anal. Calcd. for C₅H₁₂N₂O₄: C, 40.90; H, 6.87; N, 15.90.
Found: C, 41.16; 41.18; H, 6.89, 7.11;
N, 15.83, 15.80.

25. REDUCTION OF 1-NITROPROPENE WITH LITHIUM BOROHYDRIDE; 1-NITROPROPANE, 2-METHYL-1,3-DINITROPENTANE (COMPLETED EXPERIMENT).

A solution of 1-nitropropane (15.2 g., 0.175 mole) in ethyl ether (25 ml.) was added dropwise in 3 hours to a stirred suspension of lithium borohydride (1.92 g., 0.088 mole) in ethyl ether (175 ml.) contained in a 500 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at $-70^\circ \pm 1^\circ$; after addition was completed the mixture was stirred for 2 hours at -70° . The mixture was then acidified in 1 hour at 0° with urea-acetic acid solution (140 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and concentration of the filtrate on a steam bath, distillation gave: (a) 1-nitropropane (7.77 g., 0.0873 mole, 49.9%) as a colorless liquid, b.p. 65-69.5° (100 mm.), n_D^{20} 1.4035-1.4045, d_4^{20} 0.9989; MR_D (calcd.) 21.68, MR_D (found) 22.12; lit.¹⁴ b.p. 132°, d_4^{20} 1.003, n_D^{20} 1.4015, (b) crude 2-methyl-1,3-dinitropentane (0.37 g., 0.0021 mole, 2.4%) as a yellow liquid, b.p. ca. 105° (1 mm.), n_D^{20} 1.4577 and (c) a brown residue (0.9 g.).

The structure of 1-nitropropane was proven by its conversion to propionaldehyde via the Nef reaction followed by preparation of propionaldehyde 2,4-dinitrophenylhydrazone, m.p. 153.5-155.5°. The melting point of the derivative was not depressed when mixed with an authentic sample.

An infrared spectrum of the 1-nitropropane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a mononitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

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26. REDUCTION OF 2-NITRO-1-BUTENE WITH SODIUM TRIMETHOXYBOROHYDRIDE;
2-NITROBUTANE, 3-METHYL-3,5-DINITROHEPTANE (COMPLETED EXPERIMENT).

Procedure 1. A solution of 2-nitro-1-butene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added dropwise in 70 minutes to a stirred suspension of sodium trimethoxyborohydride (28.8 g., 0.15 mole plus 50% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 500 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at -60 to -65° . The mixture was then acidified in one hour at 0° with urea-acetic acid solution (100 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and evaporation of the solvent on a steam bath, distillation of the product gave the following fractions: (1) 2-nitrobutane (6.95 g., 0.0675 mole, 45%) as a colorless liquid, b.p. $60-70^{\circ}$ (80 mm.), n_D^{20} 1.4048-1.4050, d_{20}^{20} 0.9652; MR_D (calcd.) 26.33, MR_D (found) 26.19; lit.¹⁵ b.p. 140° , d_{20}^{20} 0.968, n_D 1.4036, and (2) 3-methyl-3,5-dinitroheptane (5.34 g., 0.0262 mole, 35%), b.p. $86-90^{\circ}$ (0.5 mm.), n_D^{20} 1.4568-1.4577 and (3) a residue (1.3 g.).

An infrared spectrum of Fraction 1. 2-nitrobutane (sandwich cell), contained a strong band for an aliphatic mononitro group (6.4 microns); no other functional groups were evident. The structure of 2-nitrobutane was established by its conversion to methyl ethyl ketone via the Nef reaction followed by preparation of methyl ethyl ketone 2,4-dinitrophenylhydrazone, m.p. $113.5-114^{\circ}$. The melting point of the derivative was not depressed when mixed with an authentic sample.

Redistillation of Fraction 2 gave purer 3-methyl-3,5-dinitroheptane in slightly lower yield, b.p. $79-81^{\circ}$ (0.7 mm.), n_D^{20} 1.4573, d_{20}^{20} 1.1124; MR_D (calcd.) 50.61, MR_D (found) 50.03. An infrared spectrum of the 3-methyl-3,5-dinitroheptane contained a strong band for a mononitro group (6.4 microns) and a very weak band for a carbonyl group (5.8 microns). The following analysis was obtained for the 3-methyl-3,5-dinitroheptane:

Anal. Calcd. for $C_8H_{15}N_2O_4$: C, 47.05; H, 7.90; N, 13.70.
Found: C, 47.95, 48.01; H, 7.90, 7.70;
N, 13.50, 13.35.

A derivative of 3-methyl-3,5-dinitroheptane was prepared by its conversion to 3-methyl-3-nitro-5-heptanone via the Nef reaction followed by preparation of 3-methyl-3-nitro-5-heptanone 2,4-dinitrophenylhydrazone, m.p. $131.5-132.5^{\circ}$.

Anal. Calcd. for $C_{14}H_{19}N_5O_6$: C, 47.59; H, 5.42; N, 19.82.
Found: C, 47.48; H, 5.29; N, 19.96.

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Procedure 2. The experiment was conducted as above except 2-nitro-1-butene (12.1 g., 0.12 mole) was added to sodium trimethoxyborohydride (16.9 g., 0.12 mole + 10%) in 70 minutes at -55 to -60° ; after addition was completed the mixture was stirred for 30 minutes at -60° . The ether extract was also washed with saturated sodium bisulfite solution (3 x 150 ml.). Distillation of the product gave: (a) 2-nitrobutane (5.67 g., 0.0577 mole, 29.7%) as a colorless liquid, b.p. $44-62^{\circ}$ (60 mm.), n_D^{20} 1.4047-1.4055, (b) 3-methyl-3,5-dinitroheptane (5.65 g., 0.0277 mole, 46.2%) as a yellow liquid, b.p. $99-100^{\circ}$ (1 mm.), n_D^{20} 1.4559-1.4580, and (c) a residue (1.1 g.).

Procedure 3. The experiment was conducted as previously (Procedure 1) except the 2-nitro-1-butene was added dropwise in 1.5 hours to sodium trimethoxyborohydride (21.1 g., 0.15 mole + 10% excess). During addition the reaction mixture was kept at -1 to -2° ; after addition was completed the mixture was stirred for 1.5 hours at 0° . The ether extract was also washed with sodium bisulfite solution (3 x 150 ml.). Distillation of the product gave: (a) 2-nitrobutane (1.42 g., 0.0138 mole, 9.2%) as a pale yellow liquid, b.p. $45-53^{\circ}$ (50 mm.), n_D^{20} 1.4048-1.4061, (b) 3-methyl-3,5-dinitroheptane (0.77 g., 0.00377 mole, 5.03%) as an amber liquid, b.p. $40-90^{\circ}$ (0.6 mm.), n_D^{20} 1.4570 and (c) a residue (10.41 g.).

27. REDUCTION OF 2-NITRO-1-BUTENE WITH LITHIUM BOROHYDRIDE; 2-NITROBUTANE, 3-METHYL-3,5-DINITROHEPTANE (COMPLETED EXPERIMENT).

Procedure 1. A solution of 2-nitro-1-butene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added dropwise in 3 hours to a stirred suspension of lithium borohydride (1.72 g., 0.075 mole + 5%) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 500 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at -68 to -70° ; after addition was completed the mixture was stirred for 2.5 hours at -70° . The mixture was then acidified in one hour at 0° with urea-acetic acid solution (75 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvent on a steam bath, distillation of the product gave: (1) 2-nitrobutane (9.17 g., 0.089 mole, 59.3%) as a colorless liquid, b.p. $67-70^{\circ}$ (80 mm.), n_D^{20} 1.4058-1.4098, d_{20}^{20} 0.968; MR_D (calcd.) 26.33, MR_D (found) 26.30, lit.¹⁵ b.p. 140° , d_{20}^{20} 0.968, n_D^{20} 1.4036, (2) 3-methyl-3,5-dinitroheptane (2.16 g., 0.0106 mole, 14.2%), b.p. $72-92^{\circ}$ (1.4 mm.), n_D^{20} 1.4564, and (3) a brown residue (1.4 g.).

Redistillation of Fraction 1 gave very pure colorless 2-nitrobutane, b.p. $136-137^{\circ}$ (742 mm.), n_D^{20} 1.5053; lit.¹⁵ b.p. 140° , n_D^{20} 1.4036. Its infrared spectrum (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a mononitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.6 microns).

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The structure of 2-nitrobutane was proven by its conversion to methyl ethyl ketone via the Nef reaction¹⁶ followed by preparation of methyl ethyl ketone 2,4-dinitrophenylhydrazone, m.p. 115-116.5°. The melting point of the derivative was not depressed when mixed with an authentic sample.

Procedure 2. - The experiment was conducted as above except 0.86 g., 0.0375 mole of lithium borohydride was used. Distillation of the product gave: (a) 2-nitro-1-butene (3.60 g., 0.0356 m., 23.7%) and 2-nitrobutane (6.03 g., 0.0585 mole, 39%) as a mixture (analyzed by refractive index), b.p. 53-70° (82-83 mm.), (b) crude 3-methyl-3,5-dinitroheptane (1.41 g., 0.0069 mole, 9.2%), b.p. 55-92° (1.3 mm.), n_D^{20} 1.4525, and (c) a brown residue (1.8 g.).

Procedure 3. - The experiment was conducted as above (Procedure 1) except the 2-nitro-1-butene solution was added to lithium borohydride (0.86 g., 0.0375 mole) in 1.5 hours. During addition the mixture was kept at -1 to +1°; after addition was completed the mixture was stirred for 1 hour at 0°. Distillation of the product gave: (a) 2-nitro-1-butene (3.07 g., 0.0304 mole, 20.3%) and 2-nitrobutane (2.50 g., 0.0243 mole, 16.2%) as a mixture (analysis by refractive index), b.p. 60-70° (80 mm.), (b) 3-methyl-3,5-dinitroheptane (3.49 g., 0.0171 mole, 22.8%), b.p. 96-98° (1.3 mm.), n_D^{20} 1.4594, and (c) a brown residue (2.4 g.).

Procedure 4. The experiment was conducted as above (Procedure 1) except the 2-nitro-1-butene solution was added to the lithium borohydride (0.86 g., 0.0375 mole) in 50 minutes. During addition the reaction mixture was kept at -50 to -55°; after addition was completed the mixture was stirred for 15 min. at -55°. The combined ether extract was also washed with saturated sodium bisulfite solution (3 x 200 ml., 5 minutes with each portion). Distillation of the product gave: (a) 2-nitro-1-butene (0.78 g., 0.0077 mole, 5.13%) and 2-nitrobutane (3.72 g., 0.0361 mole, 24%) as a mixture (analysis by refractive index), b.p. 63-70° (80 mm.), (b) 3-methyl-3,5-dinitroheptane (0.89 g., 0.00432 mole, 5.76%), b.p. 89-91.5° (1.2 mm.), n_D^{20} 1.4503, and (c) a black residue (0.5 g.).

28. REDUCTION OF 2-NITRO-2-BUTENE WITH SODIUM TRIMETHOXYBOROHYDRIDE;
2-NITROBUTANE, 3,4-DIMETHYL-2,4-DINITROHEXANE.

Procedure 1. A solution of 2-nitro-2-butene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added dropwise in 65 minutes to a stirred suspension of sodium trimethoxyborohydride (28.8 g., 0.15 mole, +50% excess) in ethyl ether (150 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at -70°; after addition was completed the mixture was stirred for 35 minutes at -70°. The mixture was then warmed to ca. -20°; suddenly a grey precipitate separated and the temperature rose to ca. +20°. The mixture was cooled to 0° and acidified in 1.5 hours at 0° with urea-acetic acid solution (100 ml.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over

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anhydrous sodium sulfate. The sodium sulfate was removed by filtration; distillation gave: (1) 2-nitrobutane (9.49 g., 0.0939 mole, 62.6%) as a colorless liquid, b.p. 70-73° (80 mm.), n_D^{20} 1.4038-1.4057, d_4^{20} 0.9674; MR_D (calcd.) 26.33, MR_D (found) 26.13; lit.¹⁵ b.p. 140°, d_4^{20} 0.968, n_D^{20} 1.4036, (2) 3,4-dimethyl-2,4-dinitrohexane (1.74 g., 0.0035 mole, 11.4%) as a green liquid, b.p. 111-112° (1.3 mm.), n_D^{20} 1.4642-1.4647, and (3) a residue (0.8 g.).

An infrared spectrum of the 2-nitrobutane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a mononitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

The structure of 2-nitrobutane was proven by its conversion to methyl ethyl ketone via the Nef reaction¹⁶ followed by preparation of methyl ethyl ketone 2,4-dinitrophenylhydrazone, m.p. 115-116.5°. The melting point of the derivative was not depressed when mixed with an authentic sample.

Fraction 2 was redistilled twice to give 3,4-dimethyl-2,4-dinitrohexane as a light yellow liquid in only slightly lower yield, b.p. 78-80° (0.1 mm.), n_D^{20} 1.4657, d_4^{20} 1.126; MR_D (calcd.) 50.61; MR_D (found) 50.20. Its infrared analysis indicated the presence of an aliphatic mononitro group (6.4 microns).

Anal. Calcd. for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.90; N, 13.70.
Found: C, 47.01, 47.17; H, 7.81, 8.00;
N, 13.82, 13.66.

Procedure 2. The experiment was conducted as previously except the sodium trimethoxyborohydride was suspended in 280 ml. of ethyl ether. The same rapid rise in temperature was noted when the reaction mixture was warmed to -30°. Distillation of the product gave: (a) 2-nitro-2-butene (3.19 g., 0.0316 mole, 21%) and 2-nitrobutane (9.72 g., 0.0942 mole, 62.8%) as a mixture (analysis by refractive index), b.p. 72.5-78° (80 mm.), and (b) a residue (0.5 g.).

Procedure 3. The experiment was conducted as previously (Procedure 1) except the sodium trimethoxyborohydride was suspended in 200 ml. of ethyl ether. The olefin was added in 75 minutes and, after addition was completed, the mixture was stirred for 125 minutes. The same rapid temperature rise was noted when the reaction mixture was warmed to -30°. Distillation of the product gave: (a) 2-nitro-2-butene (2.53 g., 0.0251 mole, 16.7%) and 2-nitrobutane (9.56 g., 0.0928 mole, 61.9%) as a mixture (analysis by refractive index), b.p. 72-80° (80 mm.), and (b) a residue (0.6 g.).

29. REDUCTION OF OMEGA-NITROSTYRENE WITH SODIUM TRIMETHOXYBOROHYDRIDE;
1-NITRO-2-PHENYLETHANE; 1,3-DINITRO-2,4-DIPHENYLBUTANE.

A solution of omega-nitrostyrene (14.9 g., 0.1 mole) in ethyl ether (50 ml.) and tetrahydrofuran (50 ml.) was added dropwise in 95 minutes to a stirred suspension of sodium trimethoxyborohydride (19.2 g., 0.1 mole + 50%

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excess) in ethyl ether (125 ml.) and tetrahydrofuran (25 ml.). During addition the mixture was kept at $-40 \pm 2^\circ$; after addition was completed the mixture was stirred for 25 minutes at -40° . The mixture was then acidified in 40 minutes below 0° with urea-acetic acid solution (70 ml., aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.). A solid (A) began to separate in the ether phase; the solid (A) was centrifuged, filtered and dried to give a milky-white material (2.96 g.), m.p. 255° (dec.), as yet unidentified. After drying the ether layer over anhydrous sodium sulfate and removal of the solvents on a steam bath, distillation gave: 1-nitro-2-phenylethane (5.83 g., 0.0386 mole, 38.6%) as a colorless liquid, b.p. $73-74.5^\circ$ (0.5 mm.), n_D^{20} 1.5266-1.5273, d_4^{20} 1.1314; MR_D (calcd.) 41.37, MR_D (found), 41.08; lit.¹⁷ b.p. $128-135^\circ$ (14 mm.); lit.¹⁷ b.p. $249-251^\circ$ (763 mm.); lit.¹⁷ $125-135^\circ$ (1 mm.), and (2) a distillation residue (5 g.). The infrared spectrum of 1-nitro-2-phenylethane (sandwich cell) contained bands for a mononitro group (6.35 microns) and a mono-substituted benzene ring (13.3 and 14.3 microns).

Solid A is insoluble in ether, Skellysolves, benzene, methanol, ethanol, water, carbon tetrachloride, chloroform, acetone, and acetic acid at their boiling points. Its infrared spectrum in Nujol exhibits strong bands for a mononitro group (6.4 microns) and a mono-substituted benzene ring (13.6 and 14.55 microns). Oxidation of the solid with alkaline sodium permanganate gave benzoic acid. The solid dissolves in warm ethanolic sodium hydroxide to yield a dark red solution; however, under conditions of the Nef reaction, the reaction mixture did not yield a derivative when treated with 2,4-dinitrophenylhydrazine. Analysis of the solid, presumably one of the racemic pairs of the structure: 2,4-diphenyl-1,3-dinitrobutane gave the following:

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33.
Found: C, 63.90, 63.83; H, 5.22, 5.13;
N, 9.53, 9.24.

The distillation residue (5 g.) crystallized to a pasty, amber solid; the residue was then dissolved in boiling ethanol. A white solid (B) separated from the ethanol solution on cooling; recrystallization from hot ethanol gave 1,3-dinitro-2,4-diphenylbutane (3.57 g., 0.0118 mole, 23.6%) as white plates, m.p. $120.5-121.0^\circ$. Its infrared spectrum (0.2 molar in chloroform) contained bands for a mononitro group (4.0 microns) and a mono-substituted benzene ring (14.4 microns).

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33.
Found: C, 63.90, 63.83; H, 5.22, 5.13;
N, 9.53, 9.24.

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30. REACTION OF 1-NITRO-2-PHENYLETHANE AND OMEGA-NITROSTYRENE;
1,3-DINITRO-2,4-DIPHENYLBUTANE.

A solution of omega-nitrostyrene (2.98 g., 0.02 mole) in ethyl ether (20 ml.) was added dropwise in 30 minutes to a solution of 1-nitro-2-phenylethane (5.02 g., 0.02 mole) and Triton B (1 ml.) in ethyl ether (20 ml.) and methanol (5 ml., enough to make the reaction mixture homogeneous). During addition the mixture was kept at 0°; after addition was completed the mixture was stirred at 5° for 1.5 hours. The mixture was acidified with 2 N hydrochloric acid (3 ml.). During reaction a white solid formed; this solid (2.71 g.) was filtered and air dried. The filtrate was saved.

The white solid isolated is insoluble in all common organic solvents. Its melting point, ca. 255-260°, is not depressed when it is mixed with a sample of substance A isolated from reduction of omega-nitrostyrene with sodium trimethoxyborohydride. It is tentatively assumed that this product is of the structure: 1,3-dinitro-2,4-diphenylbutane.

The filtrate that had been saved was reduced to a volume of 3-4 ml. and then dissolved in ethyl ether (50 ml.). The ether solution was washed with saturated sodium bicarbonate solution (50 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvent on a steam bath, distillation gave: (1) 1-nitro-2-phenylethane (1.62 g., 0.0107 mole, 53.5% recovery), b.p. 84-85° (1.2 mm.), n_D^{20} 1.5270; and (2) a residue (1.5 g.).

The unidentified white solid isolated in this reaction is insoluble in all common organic solvents. The melting point, ca. 255-260°, is not depressed when mixed with a sample of the unidentified white solid isolated in the reaction of sodium trimethoxyborohydride with omega-nitrostyrene.

31. PREPARATION OF 4-NITRO-3-HEPTENE.

(a) 4-Nitro-3-Heptanol. Propanal (116.2 g., 2 moles) was added at 30-35° in ca. one hour to a solution of 1-nitrobutane (106.2 g., 2 moles) in 95% ethanol (200 ml.) and 10 N sodium hydroxide (4 ml.). When approximately two thirds of the aldehyde had been added, additional 10 N sodium hydroxide (4 ml.) in water (15 ml.) was added. After 48 hours the mixture was neutralized with 2 N hydrochloric acid. After removal of all unreacted material and solvents on a steam bath and under vacuum, distillation gave: 4-nitro-3-heptanol (248.3 g., 1.54 moles, 77%) as a greenish-yellow liquid, b.p. 79.8-83.3° (0.7 mm.), n_D^{20} 1.4460-1.4474. Redistillation of the compound gave a pure, light yellow product, b.p. 71-71.5° (0.5 mm.), n_D^{20} 1.4475, d_4^{20} 1.0324; MR_D (calcd.) 41.79, MR_D (found) 41.76.

Anal. Calcd. for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69.
Found: C, 52.62, 52.73; H, 9.42, 9.41;
N, 8.45, 8.53.

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An infrared spectrum of 4-nitro-3-heptanol (sandwich cell) contained bands for the mononitro (6.4 microns) and hydroxyl (2.9 microns) groups.

(b) 3-Acetoxy-4-Nitroheptane. Acetic anhydride (129 ml., 1.2 moles + 5% excess) was added dropwise in 80 minutes at 40-50° to 4-nitro-3-heptanol (197.4 g., 1.2 moles) containing sulfuric acid (1 ml.). After addition was completed, the mixture was stirred for 2 hours. The mixture was diluted with ethyl ether (200 ml.), washed with water (2 x 100 ml.), neutralized with sodium bicarbonate, washed with saturated sodium bicarbonate solution (2 x 200 ml.), washed with sodium chloride solution (100 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 3-acetoxy-4-nitroheptane (216.9 g., 1.07 moles, 89%) as a light yellow liquid, b.p. 75.5-79° (1 mm.), n_D^{20} 1.4339-1.4362. Redistillation of the compound gave a very pure, colorless product, b.p. 69° (0.1 mm.), n_D^{20} 1.4352, d_4^{20} 1.0409; MR_D (calcd.) 51.12, MR_D (found) 50.97.

Anal. Calcd. for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89.
Found: C, 53.32; 53.21; H, 8.27, 8.38;
N, 6.86, 6.90.

An infrared spectrum of 3-acetoxy-4-nitroheptane (sandwich cell) contained bands for carbonyl (5.7 microns), mononitro(6.4 microns), and acetate (8.1 microns) groups.

(c) 4-Nitro-3-Heptene. 3-Acetoxy-4-nitroheptane (131.5 g., 0.65 mole) and sodium acetate (6.6 g.) were heated at 115° (12 mm.) in a modified Claisen flask equipped with a 20 cm. Vigreux column with downward condenser and iced receiver; the reaction product distilled at 75-85° (12 mm.). The distillate in ethyl ether (300 ml.) was washed with saturated sodium bicarbonate solution (2 x 200 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 4-nitro-3-heptene (67.6 g., 0.473 mole, 72.8%) as a light green, lachrymatory liquid, b.p. 70-70.8° (5.2 mm.), n_D^{20} 1.4564-1.4585.

An infrared spectrum of 4-nitro-3-heptene (sandwich cell) contained a strong band for a nitro group attached to an unsaturated carbon atom and weak bands for a mononitro group (6.4 microns) attached to a saturated carbon atom and for a carbon-carbon double bond. The contaminant is probably 4-nitro-2-heptene produced in the deacetylation reaction.

32. REDUCTION OF 4-NITRO-3-HEPTENE WITH SODIUM TRIMETHOXYBOROHYDRIDE;
4-NITROHEPTANE.

Procedure 1. A solution of 4-nitro-3-heptene (15.75 g., 0.11 mole) in ethyl ether (25 ml.) was added dropwise in 3 hours to a stirred suspension of sodium trimethoxyborohydride (21.11 g., 0.11 mole, plus 50% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.). During addition the

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reaction mixture was kept at $0^{\circ} \pm 1^{\circ}$; after addition was completed the mixture was stirred for 3 hours at 0° . The mixture was then acidified below 0° in one hour with urea-acetic acid solution (75 ml., aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.) and dried over anhydrous sodium sulfate. After removal of sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: (a) 4-nitroheptane (8.80 g., 0.0606 mole, 55%) as a light yellow liquid, b.p. $68-71^{\circ}$ (8.3 mm.), n_D^{20} 1.4236-1.4282; (b) a mixture of 4-nitro-3-heptene and 4-nitroheptane (1.30 g.), b.p. 72° (8.3 mm.), n_D^{20} 1.4330; and (c) an unidentified product (1.70 g.), b.p. $77-83^{\circ}$ (1.1 mm.), n_D^{20} 1.4465-1.4499. Two redistillations of the 4-nitroheptane gave a very pure, colorless product in slightly lower yield, b.p. $70-71^{\circ}$ (9 mm.), n_D^{20} 1.4224-1.4236, d_4^{20} 0.9269; MR_D (calcd.) 40.27, MR_D (found) 39.92; lit.¹⁸ b.p. 90° (25 mm.), n_D^{25} 1.4200, d_4^{25} 0.919.

An infrared spectrum of the 4-nitroheptane (sandwich cell) contained a strong band for the mononitro group (6.4 microns). An infrared spectrum of the unidentified product (sandwich cell) contained a strong band for the mononitro group (6.4 microns) and weak bands for a carbonyl group (5.8 microns) and amino group (2.93 and 6.1 microns); further studies of this product are now in progress.

The structure of 4-nitroheptane was proven by its conversion to 4-heptanone via the Nef¹⁶ reaction followed by preparation of 4-heptanone 2,4-dinitrophenylhydrazone in 45% overall yield, m.p. $74-75.5^{\circ}$. The melting point of the derivative was not depressed when mixed with an authentic sample.

Procedure 2. The experiment was conducted as previously except the nitroolefin was added in 70 minutes at 0° and the mixture was stirred for 30 minutes at 0° . Distillation gave: 4-nitro-3-heptene (4.89 g., 0.0342 mole, 31%) and 4-nitroheptane (8.07 g., 0.0555 mole, 50.5%) as a mixture, b.p. $67-80^{\circ}$ (9 mm.), n_D^{20} 1.4215-1.4497. The reaction time in this experiment was too short to effect complete reduction.

Procedure 3. The experiment was conducted as previously except the nitroolefin was added in 70 minutes at -40° and the mixture was stirred at -40° for 30 minutes. Distillation gave: 4-nitro-3-heptene (4.38 g., 0.0306 mole, 27.9%) and 4-nitroheptane (6.48 g., 0.0446 mole, 40.5%) as a mixture, b.p. $69-81^{\circ}$ (9 mm.), n_D^{20} 1.4259-1.4570. The reaction time in this experiment was too short for complete reduction.

33. REDUCTION OF 4-NITRO-3-HEPTENE WITH LITHIUM BOROHYDRIDE; 4-NITROHEPTANE.

Procedure 1. A solution of 4-nitro-3-heptene (15.75 g., 0.11 mole) in ethyl ether (25 ml.) was added dropwise in 4 hours to a stirred suspension of lithium borohydride (1.18 g., 0.055 mole) in ethyl ether (125 ml.) and tetrahydrofuran (25 ml.). During addition the reaction mixture was

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kept at -65 to -70° ; after addition was completed the mixture was stirred for 4 hours at -65 to -70° . The mixture was then acidified in 45 minutes below 0° with urea-acetic acid solution (100 ml., aqueous solution, 2.78 molal in urea and in acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: (a) a mixture of 4-nitroheptane and 4-nitro-3-heptene (12.16 g.) as a light yellow liquid, b.p. $69.3-71.3^{\circ}$ (8-8.2 mm.), n_D^{20} 1.4217-1.4319; and (b) a light yellow liquid (1.55 g.), b.p. $53-75^{\circ}$ (1 mm.), n_D^{20} 1.4450-1.4520, as yet unidentified. The mixture of 4-nitro-3-heptene and 4-nitroheptane was purified upon solution in ethyl ether (100 ml.) by extraction with saturated sodium bisulfite solution (3 x 75 ml., 5 minutes with each portion); the ether layer was then dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 4-nitroheptane (10.39 g., 0.0715 mole, 65%), n_D^{20} 1.4223-1.4234, d_4^{20} 0.9249; MR_D (calcd.) 40.27, MR_D (found) 39.99; lit.¹⁸ b.p. 90° (25 mm.), n_D^{20} 1.4200, d_4^{25} 0.919.

An infrared spectrum of the 4-nitroheptane (sandwich cell) contained a band for the mononitro group (6.4 microns). Infrared spectra of the high boiling product (b; collected in 4 fractions) showed the presence of a mononitro group (6.4 microns), a nitro group attached to a carbon atom of a carbon-carbon double bond (6.5 microns), a carbonyl group (5.7 microns) and possibly an amino group (3.0 and 6.2 microns); further characterization of this material is yet to be effected.

Procedure 2. The experiment was conducted as previously except the nitroolefin was added in 3.5 hours at 0° and then the mixture was stirred at 0° for 2 hours. Distillation gave: (a) crude 4-nitroheptane (6.57 g., 0.0452 mole, 44.7%) as a colorless liquid, b.p. $68.8-71^{\circ}$ (8.1-8.3 mm.), n_D^{20} 1.4250-1.4273; (b) an unidentified liquid (2.3 g.), b.p. $71-75^{\circ}$ (4.1-5.2 mm.), n_D^{20} 1.4419-1.4478; and (c) an unidentified liquid (1.0 g.), b.p. $60-64^{\circ}$ (0.2-0.3 mm.), n_D^{20} 1.4492-1.4507.

An infrared spectrum of the 4-nitroheptane (sandwich cell) contained a strong band for the mononitro group (6.4 microns). An infrared spectrum of product (b) contained a very weak band for a mononitro group (6.4 microns) and a medium strong band for a hydroxyl group. An infrared spectrum of product (c) contained a band for an amino group (3.1 and 6.2 microns), but no band for a mononitro group (6.4 microns). On the basis of infrared results it is suggested that product (b) is di-n-propylhydroxylamine and that product (c) is 4-aminoheptane; further studies of this system are now in progress.

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34. REDUCTION OF 3,3,3-TRICHLORO-1-NITROPROPENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 1,1,1-TRICHLORO-3-NITROPROPANE; 1,1,1-TRICHLORO-3,5-DI-NITRO-4-TRICHLOROMETHYLPENTANE.

A solution of 3,3,3-trichloro-1-nitropropene (15.20 g., 0.08 mole) in ethyl ether (25 ml.) was added dropwise in 70 minutes to a stirred suspension of sodium trimethoxyborohydride (15.3 g., 0.08 mole + 50% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at $-40^{\circ} \pm 2^{\circ}$; after addition was completed the mixture was stirred for 30 minutes at -40° . The mixture was then acidified in 45 minutes below 0° with urea-acetic acid solution (50 ml., aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, the mixture was set in a refrigerator for 3 days. A crystalline solid separated from the reaction mixture during this period. The solid was filtered and washed with methanol (5 ml.); the methanol washings were concentrated using a steam bath. The oily residue was placed in a refrigerator and allowed to crystallize. By repeating the previously described procedure, three crops of a crystalline solid were obtained: (1) 2.58 g., m.p. $150-151^{\circ}$; (2) 1.33 g., m.p. $149-150^{\circ}$; and (3) 0.62 g., m.p. $149-150^{\circ}$.

The filtrates from the above crystallizations were distilled (I) and gave: 1,1,1-trichloro-3-nitropropane (6.77 g., 0.0354 mole, 44.2%) as a colorless liquid, b.p. $91-92^{\circ}$ (9 mm.), n_D^{20} 1.4886-1.4900. Redistillation of the product gave a material of analytical purity, b.p. $70-71.3^{\circ}$ (3 mm.), n_D^{20} 1.4899, d_4^{20} 1.5347; MR_D (calcd.) 36.13, MR_D (found) 36.25.

Anal. Calcd. for $C_3H_4Cl_3NO_2$: C, 18.72; H, 2.10; N, 7.28.
Found: C, 19.11, 19.10; H, 2.13, 2.30;
N, 7.11, 7.14.

The residue (2.3 g.) from the initial distillation (I) of 1,1,1-trichloro-3-nitropropane was dissolved in hot methanol (10 ml.); the mixture was then cooled in a refrigerator and gave an additional crop (4; 0.38 g.) of the white crystalline solid, m.p. $147-148^{\circ}$. The crops of solids were combined and recrystallized twice from hot carbon tetrachloride to give a product identified as 1,1,1-trichloro-3,5-dinitro-4-trichloromethylpentane (4.0 g., 0.01285 mole, 32.1%), a white fibrous material, m.p. $150-151^{\circ}$.

Anal. Calcd. for $C_6H_6Cl_3N_2O_4$: C, 18.82; H, 1.58; N, 7.32.
Found: C, 18.79, 18.76; H, 1.72, 1.71;
N, 7.30, 7.26.

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The infrared spectrum of 1,1,1-trichloro-3-nitropropane (sandwich cell) contained strong bands for a mononitro group (6.35 microns), a trichloromethyl group (12.5 microns) and a carbon-chlorine bond (14.4 microns). The infrared spectrum of 1,1,1-trichloro-3,5-dinitro-4-trichloromethylpentane (0.2 molar in chloroform) contained strong bands for a mononitro group (6.35 microns) and a trichloromethyl group (12.4 microns).

35. REDUCTION OF 3,3,3-TRICHLORO-1-NITROPROPENE WITH LITHIUM BOROHYDRIDE;
1,1,1-TRICHLORO-3-NITROPROPANE.

Procedure 1. A solution of 3,3,3-trichloro-1-nitropropene (30.4 g., 0.16 mole) in ethyl ether (50 ml.) was added dropwise in 3.5 hours to a stirred suspension of lithium borohydride (1.74 g., 0.08 mole) in ethyl ether (250 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at $-70^{\circ} \pm 2^{\circ}$; after addition was completed, the mixture was stirred for 3.5 hours at -70° . The mixture was then acidified below 0° in one hour with urea-acetic acid solution (150 ml., aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was extracted with ethyl ether (2 x 100 ml.). The combined ether extract was washed with saturated sodium bicarbonate, dried with sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 1,1,1-trichloro-3-nitropropane (26.09 g., 0.136 mole, 85%) as a colorless liquid, b.p. $66.7-66.8^{\circ}$ (2.1-2.3 mm.), n_D^{20} 1.4905-1.4910.

An infrared spectrum of the 3,3,3-trichloro-1-nitropropane (sandwich cell) contained strong bands for a mononitro group (6.35 microns), a trichloromethyl group (12.5 microns) and a carbon-chlorine bond (14.4 microns).

Procedure 2. The experiment was conducted as previously except one-half of all materials was used, and the 3,3,3-trichloro-1-nitropropene was added in 3.5 hours at -40° and then stirred for 2 hours at -40° . Distillation gave: 1,1,1-trichloro-3-nitropropane (7.38 g., 0.0386 mole, 48.3%) as a colorless liquid, b.p. $67-68^{\circ}$ (2.3 mm.), n_D^{20} 1.4914-1.4939. Redistillation gave a very pure product, b.p. $67-67.7^{\circ}$ (2.3 mm.), n_D^{20} 1.4905, d_4^{20} 1.5375; MR_D (calcd.) 36.13, MR_D (found) 36.22.

36. REDUCTION OF 3,3,3-TRICHLORO-1-NITROPROPENE WITH LITHIUM ALUMINUM
HYDRIDE: 1,1,1-TRICHLORO-3-NITROPROPANE.

A solution of 3,3,3-trichloro-1-nitropropene (19.0 g., 0.1 mole) in ethyl ether (25 ml.) was added dropwise in 3.5 hours to a suspension of lithium aluminum hydride (1.0 g., 0.025 mole, plus 5% excess) in ethyl ether (125 ml.) and tetrahydrofuran (25 ml.). During addition the reaction mixture was kept at -70° ; after addition was completed the mixture was stirred for 3.5 hours at -70° . The mixture was acidified in 45 minutes below 0° with urea-acetic acid solution (50 ml., 0.278 molal in urea and in acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate (2 x 150 ml.) and

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dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 1,1,1-trichloro-3-nitropropane and 3,3,3-trichloro-1-nitropropane as a mixture (13.24 g.), b.p. 61-68° (2.3 mm.), n_D^{20} 1.4929-1.5034. The above mixture in ethyl ether (150 ml.) was washed with saturated sodium bisulfite solution (3 x 150 ml., 5 minutes with each portion) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave 1,1,1-trichloro-3-nitropropane (8.43 g., 0.0438 mole, 43.8%) as a colorless liquid, b.p. 65-66.5° (2.2 mm.), n_D^{20} 1.4911-1.4923, d_4^{20} 1.5375; MR_D (calcd.) 36.13; MR_D (found) 36.28.

37. REDUCTION OF 5,5,6,6,7,7,7-HEPTAFLUORO-3-NITRO-3-HEPTENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 1,1,1,2,2,3,3-HEPTAFLUORO-5-NITROHEPTANE; 2,2,5,6,6,7,7,7-HEPTAFLUORO-3-HEPTANONE.

A solution of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene (15.34 g., 0.057 mole) in ethyl ether (25 ml.) was added dropwise in 2 hours to a stirred suspension of sodium trimethoxyborohydride (10.94 g., 0.057 mole + 50% excess) in ethyl ether (125 ml.) and tetrahydrofuran (25 ml.). During addition the reaction mixture was kept at -60 to -65°; after addition was completed the mixture was stirred for 1 hour at -60 to -65°. The mixture was then acidified in 45 minutes below 0° with urea-acetic acid solution (75 ml., aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration, distillation gave, after removal of the solvent, 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (14.07 g., 0.052 mole, 91%) as a colorless liquid, b.p. 78.5-79° (23-25 mm.), n_D^{20} 1.3485-1.3491, d_4^{20} 1.4286; lit.¹⁰ b.p. 60° (9 mm.), n_D^{20} 1.3493. The infrared spectrum of 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (sandwich cell) contained strong bands for the mononitro group (6.35 microns) and for carbon-fluorine bonds (8.0-8.5 microns).

A solution of 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (1 g., 0.00369 mole) in methanol (10 ml.) was added to a solution of sodium hydroxide (0.4 g., 0.01 mole) in water (10 ml.) and kept at 0° for 18 hours. This solution was added dropwise at 0° to concentrated sulfuric acid (2.5 ml.) in water (12 ml.); a solution of 2,4-dinitrophenylhydrazine was added. An oil separated and was crystallized from hot ethanol; four recrystallizations from hot ethanol gave 5,5,6,6,7,7,7-heptafluoro-3-heptanone 2,4-dinitrophenylhydrazone (0.71 g., 0.00185 mole, 50%) as orange needles, m.p. 123-124°.

Anal. Calcd. for $C_{12}F_7H_{11}N_4O_4$: C, 37.15; H, 2.64; N, 13.33.
Found: C, 37.75, 37.62; H, 2.99, 2.85;
N, 13.51, 13.56.

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38. REDUCTION OF 5,5,6,6,7,7,7-HEPTAFLUORO-3-NITRO-3-HEPTENE WITH LITHIUM BOROHYDRIDE; 1,1,1,2,2,3,3-HEPTAFLUORO-5-NITROHEPTANE; 5,5,6,6,7,7,7-HEPTAFLUORO-3-HEPTANONE 2,4-DINITROPHENYLHYDRAZONE.

A solution of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene (15.34 g., 0.057 mole) in ethyl ether (25 ml.) was added dropwise in 4 hours to a stirred suspension of lithium borohydride (0.62 g., 0.0285 mole) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.). During addition the reaction mixture was kept at $-60^{\circ} \pm 2^{\circ}$; after addition was completed the mixture was stirred for 4 hours at -60° . The mixture was acidified in 45 minutes below 0° with urea-acetic acid solution (75 ml., an aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (14.08 g., 0.052 mole, 91%) as a colorless liquid, b.p. $79-79.8^{\circ}$ (24.5-25 mm.), n_D^{20} 1.3488-1.3496, d_4^{20} 1.4254; lit.¹⁰ b.p. 60° (9 mm.), n_D^{20} 1.3493.

An infrared spectrum of the 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (sandwich cell) contained strong bands for the mononitro group (6.35 microns) and carbon-fluorine bonds (8.0-8.5 microns).

A solution of 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (1 g., 0.00369 mole) in methanol (10 ml.) was added to a solution of sodium hydroxide (0.4 g., 0.01 mole) in water (10 ml.) and kept at 0° for 18 hours. This solution was added dropwise at 0° to concentrated sulfuric acid (2.5 ml.) in water (12 ml.); a solution of 2,4-dinitrophenylhydrazine was then added. An oil separated which was crystallized from hot ethanol; four recrystallizations gave 5,5,6,6,7,7,7-heptafluoro-3-heptanone 2,4-dinitrophenylhydrazone (0.83 g., 0.00216 mole, 58.5%) as orange needles, m.p. $123-124^{\circ}$. The melting point was not depressed when mixed with a sample prepared in the previous experiment.

39. REDUCTION OF 5,5,6,6,7,7,7-HEPTAFLUORO-3-NITRO-3-HEPTENE WITH LITHIUM ALUMINUM HYDRIDE; 1,1,1,2,2,3,3-HEPTAFLUORO-5-NITROHEPTANE.

A solution of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene (15.34 g., 0.057 mole) in ethyl ether (25 ml.) was added dropwise in 3 hours to a stirred suspension of lithium aluminum hydride (0.65 g., 0.01625 mole + 20% excess) in ethyl ether (125 ml.) and tetrahydrofuran (25 ml.). During addition the mixture was kept at -65 to -70° ; after addition was completed the mixture was stirred at -60 to -70° for 3.5 hours. The mixture was then acidified in 35 minutes below 0° with urea-acetic acid solution (35 ml., aqueous solution, 2.78 molal in urea and in acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.) and dried

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over anhydrous sodium sulfate. Filtration, removal of solvents on a steam bath, and distillation gave: 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (13.17 g., 0.0486 mole, 85.3%) as a colorless liquid, b.p. 78.5-78.7° (23 mm.), n_D^{20} 1.3490-1.3497, d_4^{20} 1.4277; lit.¹⁰ b.p. 60° (9 mm.), n_D^{20} 1.3493.

An infrared spectrum of the 1,1,1,2,2,3,3-heptafluoro-5-nitroheptane (sandwich cell) contained strong bands for the mononitro group (6.35 microns) and the carbon-fluorine bond (8.0-8.6 microns).

40. ATTEMPTED HETEROGENEOUS REDUCTION OF 5,5,6,6,7,7,7-HEPTAFLUORO-3-NITRO-3-HEPTENE WITH SODIUM BOROHYDRIDE.

A solution of 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene (6.72 g., 0.025 mole) in ethyl ether (20 ml.) was added dropwise in 3 hours to a suspension of sodium borohydride (0.47 g., 0.0125 mole) in ethyl ether (65 ml.) and tetrahydrofuran (20 ml.). During addition the reaction mixture was kept at -65°; after addition was completed the mixture was stirred at -65° for 3.5 hours. The mixture was then acidified in 20 minutes below 0° with urea-acetic acid solution (25 ml., aqueous solution, 2.78 molal in urea and in acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (50 ml.). The ether extracts were combined and washed with saturated sodium bicarbonate solution (2 x 100 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene (5.38 g., 80% recovery), the initial olefin, as a light green liquid, b.p. 77-78° (79 mm.), n_D^{20} 1.3590-1.3597. The physical constants of the initial material, 5,5,6,6,7,7,7-heptafluoro-3-nitro-3-heptene, are: b.p. 78.5-79.5° (75 mm.), n_D^{20} 1.3596.

41. REDUCTION OF 4,4,5,5,6,6,6-HEPTAFLUORO-2-NITRO-2-HEXENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 1,1,1,2,2,3,3-HEPTAFLUORO-5-NITROHEXANE.

A solution of 5,5,6,6,7,7,7-heptafluoro-2-nitro-2-hexene (7.50 g., 0.0294 mole) in ethyl ether (25 ml.) was added dropwise in 2 hours to a stirred suspension of sodium trimethoxyborohydride (5.76 g., 0.0294 mole + 50% excess) in ethyl ether (75 ml.) and tetrahydrofuran (25 ml.). During addition the reaction mixture was kept at -65 to -70°; after addition was completed the mixture was stirred for one hour at -65 to -70°. The mixture was then acidified in 30 minutes below 0° with urea-acetic acid solution (25 ml., aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 75 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 1,1,1,2,2,3,3-heptafluoro-5-nitrohexane (6.34 g., 0.0247 mole, 84%) as a colorless liquid, b.p. 77-78.8° (39-40 mm.), n_D^{20} 1.3405-1.3409, d_4^{20} 1.4861; lit.¹⁰ b.p. 64° (23 mm.), n_D^{20} 1.3412. An

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infrared spectrum of the 1,1,1,2,2,3,3-heptafluoro-5-nitrohexane contained a strong band for the mononitro group (6.35 microns) and for carbon-fluorine bonds (8.0-8.4 microns).

42. REDUCTION OF 4,4,5,5,6,6,6-HEPTAFLUORO-2-NITRO-2-HEXENE WITH LITHIUM BOROHYDRIDE; 1,1,1,2,2,3,3-HEPTAFLUORO-5-NITROHEXANE.

A solution of 4,4,5,5,6,6,6-heptafluoro-2-nitro-2-hexene (7.50 g., 0.0294 mole) in ethyl ether (25 ml.) was added dropwise in 4 hours to a stirred suspension of lithium borohydride (0.33 g., 0.015 mole) in ethyl ether (75 ml.) and tetrahydrofuran (25 ml.). During addition the reaction mixture was kept at $-65^{\circ} \pm 2^{\circ}$; after addition was completed the mixture was stirred for 4 hours at -65 to -70° . The mixture was then acidified in 30 minutes below 0° with urea-acetic acid solution (35 ml., aqueous solution, 2.78 molal in urea and acetic acid). The mixture was saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 100 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of the solvents on a steam bath, distillation gave: 1,1,1,2,2,3,3-heptafluoro-5-nitrohexane (6.64 g., 0.0258 mole, 87.8%) as a colorless liquid, b.p. $76.5-77.5^{\circ}$ (38 mm.), n_D^{20} 1.3405-1.3410, d_4^{20} 1.4861; lit.¹⁰ b.p. 64° (23 mm.), n_D^{20} 1.3412. An infrared spectrum of the 1,1,1,2,2,3,3-heptafluoro-5-nitrohexane contained a strong band for a mononitro group (6.35 microns) and for carbon-fluorine bonds (8.2 microns).

43. REDUCTION OF D-ARABO-TETRAACETOXY-1-NITROHEXENE; 1-NITRO-1,2-DIDESOXY-D-ARABO-HEXITOL TETRAACETATE.

A solution of D-arabo-tetraacetoxy-1-nitro-1-hexene (1.01 g., 0.0028 mole) in absolute ethanol (10 ml.) was added dropwise in 45 minutes to a stirred suspension of sodium borohydride (0.12 g., 0.0014 mole) in absolute ethanol (10 ml.). During addition the mixture was kept at 0° ; after addition was completed the mixture was stirred for 2 hours at 0° . The mixture was then acidified below 0° in 10 minutes with urea-acetic acid solution (3 ml., 0.278 molal in acetic acid and in urea). The reaction mixture was reduced to a volume of about 5 ml. on a steam bath and under vacuum. This mixture was taken up in ethyl ether (40 ml.), washed with saturated sodium bicarbonate solution (2 x 15 ml.) and dried over anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and removal of all but 2-3 ml. of solvent, 1-nitro-1,2-didesoxy-D-arabo-hexitol tetraacetate (0.65 g., 0.00179 mole, 65.9%) crystallized as a white solid, m.p. $82-84^{\circ}$. One recrystallization from absolute ether gave only a slightly lower yield of highly pure product, m.p. $115-116^{\circ}$; lit.¹⁹ m.p. $115-116^{\circ}$.

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Note: In submitting this report it is understood that all provisions of the contract between the Foundation and the Cooperator and pertaining to publicity of subject matter will be rigidly observed.

Investigators:

L. E. Lay & D. C. Iffland
E. B. Robinson, I. H. Morrison

Date May 28, 1954

Supervisor

H. Shetter

Date May 28, 1954

FOR THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION

Executive Director

Ernest C. Woolpert

Date May 28, 1954

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